



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09K 11/06, H05B 33/14, C07F 5/06	A1	(11) International Publication Number: WO 98/36035 (43) International Publication Date: 20 August 1998 (20.08.98)
(21) International Application Number: PCT/CA98/00100 (22) International Filing Date: 13 February 1998 (13.02.98) (30) Priority Data: 60/039,688 13 February 1997 (13.02.97) US 60/044,037 30 May 1997 (30.05.97) US (71) Applicant: QUEEN'S UNIVERSITY AT KINGSTON [CA/CA]; Queen's University, Kingston, Ontario K7L 3N6 (CA). (72) Inventors: WANG, Suning; 129 Robert Wallace Drive, Kingston, Ontario K7M 1Y2 (CA). LIU, Wang; Suite 908, 40 Fountain Head Road, North York, Ontario M3J 2V1 (CA). HASSAN, Abdi; 3647 Wells Street, Windsor, Ontario N9C 1T8 (CA). (74) Agents: STEEG, Carol, Miernicki et al.; Parteq Innovations, Queen's University, Kingston, Ontario K7L 3N6 (CA).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LUMINESCENT COMPOUNDS AND METHODS OF MAKING AND USING SAME		
(57) Abstract		
<p>The invention provides heterocyclic organoaluminum and organoboron coordination complexes that are photoluminescent and electroluminescent, emitting intense blue light. The invention further provides methods of synthesizing such compounds, methods of producing photoluminescence and electroluminescence, methods of applying the compounds in thin films, and uses of the compounds of the invention in luminescent probes, electroluminescent displays and the like.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

LUMINESCENT COMPOUNDS AND METHODS OF MAKING AND USING SAME**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is related to U.S.S.N. 60/039,688, filed February 13, 1997, and
5 U.S.S.N. 60/044,037, filed May 30, 1997, the contents of which are hereby incorporated
herein in their entirety.

FIELD OF THE INVENTION

The invention relates to compounds having luminescent properties, and to methods of
synthesizing and using such compounds. The invention more particularly relates to
10 compounds having photoluminescent and/or electroluminescent properties, and to synthesis
and uses of same.

BACKGROUND OF THE INVENTION

A variety of luminescent compounds are known in the art. Green and red luminescent
compounds are not uncommon, but blue luminescent metal ions and molecules are rare and
15 generally expensive.

Two types of blue luminescent inorganic coordination compounds are known in
which a heterocyclic chromophore includes a metal center coordinated by nitrogen and
oxygen atoms of organic ligands. One type is based on 8-hydroxyquinoline and derivatives
thereof, and the other is based on azomethine and derivatives thereof. Both the 8-
20 hydroxyquinoline- and azomethine-based systems usually require several steps of synthesis
and modification in order to achieve blue luminescence. The usefulness of these two systems
in practical electroluminescence applications is limited, and blue luminescent materials with
improved properties are desirable.

Production of devices based on electroluminescent display, and in particular on flat
25 panel display, is a rapidly growing, billion dollar industry. Blue luminescent materials, as
one of the key color components for electroluminescence display devices, are among the
most sought-after materials by industry around the world.

SUMMARY OF THE INVENTION

30 It is an object of the present invention to provide blue luminescent compounds with
improved properties. Another object of the invention is to provide improved luminescent
products including such a compound. As used herein, the term "compound" includes

coordination complexes, sometimes referred to simply as "complexes". The term "aliphatic" includes alkyl, alkenyl and alkynyl, and straight and branched chain.

The invention provides compounds having the following formulas:

- (i) $[AlR_2(azain)]_n$,
- (ii) $[AlR_2(dpa)]_n$,
- (iii) $[Al_4R_6O_2(dpa)_2]$,
- (iv) $Al(PFPA)_3$, and
- (v) derivatives of (i), (ii), (iii) and (iv),

where R is aliphatic, aryl or alkoxyl, azain is deprotonated 7-azaindole, dpa is deprotonated di-2-pyridyl amine, and PFPA is deprotonated pentafluorophenyl-2-pyridylamine. The compounds are photoluminescent and, in at least some embodiments of the invention, they are electroluminescent; they produce intense blue light.

The invention also provides compounds having the following formulas:

- (i) $Al_2R_2(azain)_4$,
- (ii) $Al_2(R)(azain)_2(OR')_3$,
- (iii) $Al_3(R)(azain)_4(OR')_2(O)$,
- (iv) $Al_3R_3(azain)_4(O)$, and
- (v) derivatives of (i), (ii), (iii) and (iv),

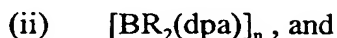
where R and R' are aliphatic, aryl or alkoxyl groups, azain is deprotonated 7-azaindole, and dpa is deprotonated di-2-pyridyl amine. The compounds are photoluminescent and, in at least some embodiments of the invention, they are electroluminescent; they produce intense blue light.

The invention further provides corresponding compounds wherein aluminum is replaced by boron. Such corresponding compounds include compounds having the following formulas:

- (i) $B(dpa)X_2$,
- (ii) $[BR_2(azain)]_n$,
- (iii) $B_2R_2(azain)_2(O)$,
- (iv) $BR_3(azainH)$, and
- (v) derivatives of (i), (ii), (iii) and (iv),

where azain is deprotonated 7-azaindole, dpa is deprotonated di-2-pyridyl amine, X is halide or alkoxyl, and R is aliphatic, aryl or alkoxyl.

Such corresponding compounds also include compounds having the following formulas:



where dpa is deprotonated di-2-pyridyl amine, and R and R' are aliphatic, aryl or alkoxy groups.

The boron compounds of the invention are photoluminescent and, in at least some embodiments of the invention, they are electroluminescent; they produce intense blue light.

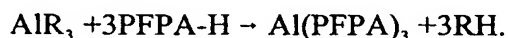
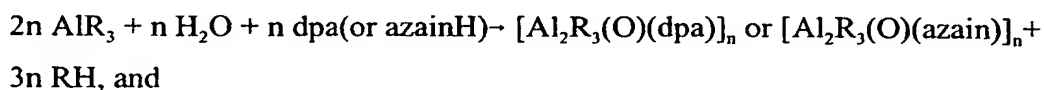
The term "derivatives" includes compounds where derivatives of 7-azaindole (e.g., phenyl-7-azaindole, methyl-7-azaindole, disubstituted compounds, and the like) and derivatives of di-2-pyridyl amine are substituents of the compounds, as discussed below. In certain embodiments of the invention, these may provide advantageous physical or chemical properties.

The invention provides a method of synthesizing a compound of the invention including the step:

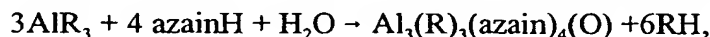
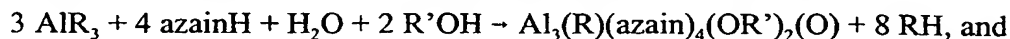
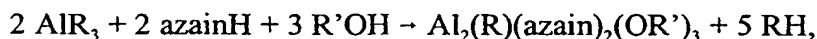
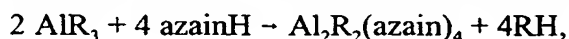


where (n = 1 or 2).

The invention further provides a method of synthesizing a compound of the invention including the step:

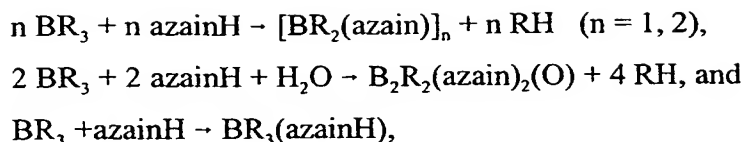


The invention also provides a method of synthesizing a compound of the invention including a step selected from the following group:



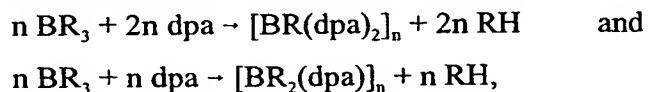
where R and R' are aliphatic, aryl or alkoxy groups.

The invention further provides a method of synthesizing a compound of the invention including a step selected from the following group:



where R and R' are aliphatic, aryl or alkoxy groups.

5 The invention also provides a method of synthesizing a compound of the invention including a step selected from the following group:



where R and R' are aliphatic, aryl or alkoxy groups.

10 The invention provides a method of producing photoluminescence comprising the steps of: providing a photoluminescent compound of the invention having a formula as set out above (or a derivative thereof); and irradiating said photoluminescent compound with radiation of a wavelength suitable for exciting the compound to photoluminesce.

15 The invention provides a method of producing electroluminescence comprising the steps of: providing an electroluminescent compound of the invention having a formula as set out above (or a derivative thereof); and applying a voltage across said electroluminescent compound.

20 The invention further provides use of a compound of the invention as a component of a photoluminescent product or an electroluminescent product. For example, a luminescent compound could be used as a luminescent probe, or as a thin film in an electroluminescent display, such as a flat panel display device.

25 The invention still further provides an electroluminescent device for use with an applied voltage, comprising: a first electrode, an emitter (i.e., phosphor) which is an electroluminescent compound of the invention, and a second, transparent electrode, wherein a voltage is applied between the two electrodes to produce an electric field across the emitter. The emitter consequently electroluminesces. In some embodiments of the invention, the device includes one or more dielectric layers interposed between the emitter and one or more of the electrodes. For example, spacing of a preferred embodiment of the device is: first electrode, first dielectric layer, emitter, second dielectric layer, and second, transparent
30 electrode.

In addition, the invention provides methods of applying compounds of the invention to a surface. These include chemical vapor deposition, spin coating and dip coating. The

compounds may be applied alone or with a carrier. In some embodiments of the invention, they are applied in a composition including an organic polymer. Such compositions are also encompassed by the invention.

5 BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the present invention and to show more clearly how it may be carried into effect, reference will now be made by way of example to the accompanying drawings, which illustrate aspects and features according to preferred embodiments of the present invention, and in which:

- 10 Figure 1 shows the excitation and emission spectra of $\text{Al}(\text{CH}_3)_2(\text{dpa})$;
Figure 2 shows the excitation and emission spectra of $\text{Al}_2(\text{CH}_3)_4(\text{azain})_2$;
Figure 3 shows the crystal structure of $\text{Al}(\text{CH}_3)_2(\text{dpa})$;
Figure 4 shows the crystal structure of $\text{Al}_2(\text{CH}_3)_4(\text{azain})_2$;
Figure 5 shows the crystal structure of $\text{Al}_4(\text{CH}_3)_6(\text{dpa})_2\text{O}_2$;
- 15 Figure 6 shows the emission spectrum of $\text{Al}_2(\text{CH}_3)_4(\text{azain})_2$ in a poly(methyl methacrylate) matrix (dashed line) and the emission spectrum of the pure poly(methyl methacrylate);
Figure 7 shows the excitation and emission spectra of $\text{Al}_4(\text{CH}_3)_6(\text{dpa})_2\text{O}_2$;
Figure 8 shows the excitation and emission spectra of $\text{Al}(\text{CH}_3)_2(\text{azain})_4$;
- 20 Figure 9 shows the crystal structure of $\text{Al}(\text{CH}_3)_2(\text{azain})_4$;
Figure 10 shows the excitation and emission spectra of
 $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$;
Figure 11 shows the crystal structure of $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$;
Figure 12 shows the excitation and emission spectra of
- 25 $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$;
Figure 13 shows the crystal structure of $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$;
Figure 14 shows the excitation and emission spectra of $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$;
Figure 15 shows the crystal structure of $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$;
Figure 16 shows the excitation and emission spectra of $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2\text{O}$;
- 30 Figure 17 shows the crystal structure of $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2\text{O}$;
Figure 18 shows the structure of 2-substituted 7-azaindole;
Figure 19 shows the crystal structure of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{Ph-azain})_4$;

Figure 20 shows the excitation and emission spectra of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{Ph-azain})_4$;

Figure 21 shows the crystal structure of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{CH}_3\text{-azain})_4$;

Figure 22 shows the excitation and emission spectra of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{CH}_3\text{-azain})_4$;

Figure 23 shows the structure of pentafluorophenyl-2-pyridylamine (PFPA-H);

Figure 24 shows the crystal structure of $\text{Al}(\text{PFPA})_3$;

Figure 25 shows the excitation and emission spectra of $\text{Al}(\text{PFPA})_3$;

Figure 26 shows the crystal structure of $\text{BPh}_3(\text{azainH})$;

Figure 27 shows the excitation and emission spectra of $\text{BPh}_3(\text{azainH})$;

Figure 28 shows the excitation and emission spectra of $\text{B}(\text{OPh})_3(\text{azain})$; and

Figure 29 shows a preferred embodiment of a electroluminescent (EL) display device according to the invention.

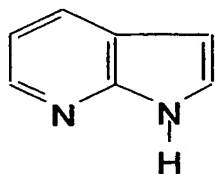
DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Two alternative ways in which a blue luminescent material could be achieved are: (i) providing a molecule which emits blue color (emitter), and (ii) doping an emitter to a suitable matrix such that the combination yields blue luminescence. The emitter can be either an inorganic metal ion such as lanthanide which emits blue light via $d \rightarrow f$ or $f \rightarrow f$ electronic transition, or an organic molecule which has conjugated π bonds and emits blue light via $\pi \rightarrow \pi$ or $\pi \rightarrow n$ electronic transitions.

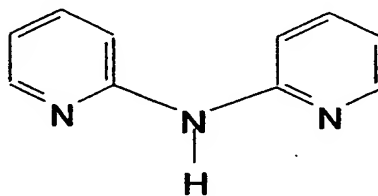
The known inorganic blue emitters, lanthanide ions, have low emission efficiency and require the use of a host (generally an inorganic salt), which makes it difficult to process them into thin films. Only a few organic blue emitters are known to date. Those known organic blue emitters are typically extended π oligomers or polymers. They are not only difficult to synthesize, thus, very expensive for an industrial scale application, but also tend to have poor luminescence efficiency and poor stability. In addition, the applications of luminescent polymers are limited, as their poor volatility prevents them being applied as films using chemical vapor deposition (CVD), a process known to produce superior films for electroluminescence displays.

We have discovered new organoaluminum and organoboron compounds that exhibit intense blue luminescence. Organoaluminum compounds of the invention include: $[\text{AlR}_2(\text{azain})]_n$, $[\text{AlR}_2(\text{dpa})]_n$, $[\text{Al}_4\text{R}_6\text{O}_2(\text{dpa})_2]$, and $\text{Al}(\text{PFPA})_3$, where R = aliphatic, aryl, alkoxyl; azain = deprotonated 7-azaindole (shown below); dpa = deprotonated di-2-pyridyl

amine (shown below); and PFPA = deprotonated pentafluorophenyl-2-pyridylamine (see Figure 23); as well as, $Al_2R_2(azain)_4$, $Al_2(R)(azain)_2(OR')_3$, $Al_3(R)(azain)_4(OR')_2(O)$, and $Al_3R_3(azain)_4(O)$, where R and R' = aliphatic, aryl, alkoxyl; azain = deprotonated 7-azaindole; dpa = deprotonated di-2-pyridyl amine. Organoboron compounds of the invention include: $B(dpa)X_2$, $[BR_2(azain)]_n$, $B_2R_2(azain)_2(O)$, and $BR_3(azainH)$, where azain = deprotonated 7-azaindole; dpa = deprotonated di-2-pyridyl amine; X = halide, alkoxyl; and R is aliphatic, aryl, alkoxyl; as well as, $[BR(dpa)_2]_n$ and $[BR_2(dpa)]_n$, where dpa = deprotonated di-2-pyridyl amine; and R and R' = aliphatic, aryl, alkoxy. Derivatives of these compounds are also encompassed by the invention. For photoluminescence, the compounds absorb energy from ultraviolet radiation and emit visible light in the blue region, i.e., near the ultraviolet end of the visible spectrum. For electroluminescence, the absorbed energy is from an applied electric field.



7-azaindole



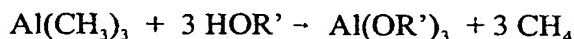
di-2-pyridyl amine

A typical reaction scheme is as follows:

$$n AlR_3 + n dpa \text{ (or azainH)} \rightarrow [AlR_2(dpa)]_n \text{ or } [AlR_2(azain)]_n + n RH$$

Here, n is 1 or 2. The aliphatic, aryl or alkoxyl group R abstracts the acidic proton from di-2-pyridyl amine (or 7-azaindole) to form alkane (RH) or alcohol (ROH), respectively. In most embodiments of the invention, the desired product is conveniently produced in a single step.

Starting materials 7-azaindole and di-2-pyridyl amine are inexpensive and readily available from commercial sources. AlR_3 can be either purchased directly from commercial sources or synthesized by a one step metathesis reaction using commercially available trialkylaluminum (e.g., $Al(CH_3)_3$) as the starting material, as follows:

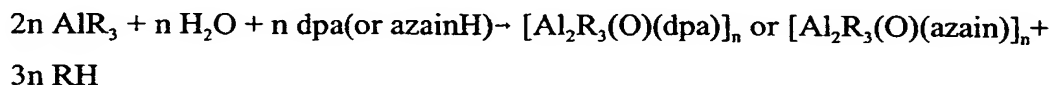


Thus, this starting material is also inexpensive and readily available.

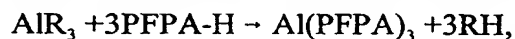
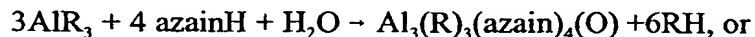
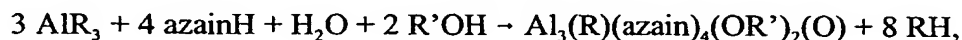
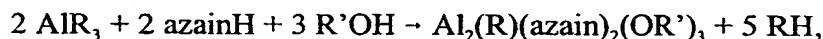
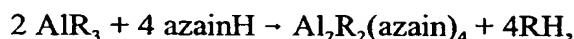
Starting material pentafluorophenyl-2-pyridylamine (PFPA-H) is also readily produced by the method of R. Koppang, *J. Organometallic Chemistry*, 46, 193 (1972) (See Example 16).

Derivatives of starting materials 7-azaindole and di-2-pyridyl amine may also be employed to produce luminescent compounds of the invention. Examples 12 and 13 below illustrate preparation of phenyl-7-azaindole and methyl-7-azaindole, respectively. As would be apparent to a person of ordinary skill in the art, other functionalities than methyl and phenyl may be included in derivatives according to the invention. For example, 7-azaindole and di-2-pyridyl amine may be substituted on one or more carbons with an aliphatic (alkyl, alkenyl or alkynyl, straight or branched chain), aromatic, alkoxy, hydroxyl, halogen, amino, nitro, or nitrile group, -CF₃, or the like. Alternatively, starting materials 7-azaindole and di-2-pyridyl amine may be modified to include, but are not limited to, functionalities such as ether, epoxide, ester, amide or the like. Such functionalities may in some cases confer desirable physical or chemical properties, such as increased stability or luminescence.

The following is another typical reaction scheme which may be employed to yield a luminescent compound of the invention:

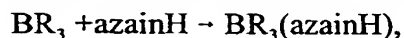
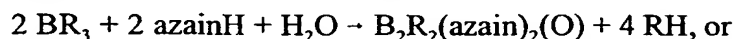
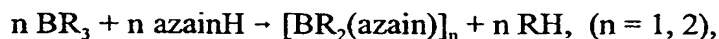


Other typical reaction schemes according to the invention include a synthesis, as follows:



where R and R' are aliphatic, such as, for example, ethyl or iso-propyl, aryl or alkoxy groups, and PFPA is deprotonated pentafluorophenyl-2-pyridylamine.

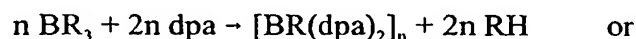
Other typical reaction schemes according to the invention include a synthesis, as follows:



where R and R' are aliphatic, such as, for example, ethyl or iso-propyl, aryl or alkoxy groups. A particularly preferred compound according to this aspect of the invention, which has been shown to exhibit blue photoluminescence and blue electroluminescence, is $B_2(C_2H_5)_2(azain)_2(O)$, for which a preferred synthetic protocol is described in Example 11.

Other particularly preferred compounds according to this aspect of the invention are $BR_3(azain)$, where R is phenyl or phenoxy (see Examples 18 and 19). These compounds also demonstrate strong photoluminescence and are easy to synthesize.

Still other typical reaction schemes according to the invention include a synthesis, as follows:



where R and R' are aliphatic, aryl or alkoxy groups.

Specific examples of syntheses according to preferred embodiments of the invention are given below in Examples 1-11.

In undertaking to achieve blue luminescent aluminum complexes with azaindole or dipyridyl amine, the inventors took into account the following physico-chemical reasoning: First, the desired compound should be colorless. As the aluminum(III) (Al(III)) ion does not have any *d* electrons and its compounds are usually colorless, the inventors reasoned that it would be a good candidate as a binding center for the organic ligands. Second, 7-azaindole and di-2-pyridyl amine can form extended π structures upon coordinating to a metal center, and thus could potentially function as emitters through $\pi \rightarrow \pi$ or $n \rightarrow \pi$ transitions.

One advantage of combining an inorganic metal ion (Al(III)) with organic ligands (dpa, azaindole) is that the luminescence efficiency of the organic chromophore is enhanced. The coordination of a metal center to an organic chromophore can increase the chromophore's structural rigidity, thereby reducing the probability of energy loss via a thermal non-radiation process and increasing the efficiency of emission. For example, we have discovered that di-2-pyridyl amine and 7-azaindole have only very weak luminescence at ambient temperature (23 °C), but upon coordinating to the aluminum center, the emission intensity increases dramatically. Both $Al(CH_3)_2(dpa)$ and $[Al(CH_3)_2(azain)]_2$ emit intense blue light as shown by their excitation and emission spectra, depicted in Figures 1 and 2. The formation of aluminum compounds with the organic ligands clearly played a key role in inducing the intense blue luminescence.

The inventors have shown that the analogous alkoxyl compounds $\text{Al}(\text{OPr}^i)_2(\text{dpa})$ and $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$, where $\text{Pr}^i = \text{iso-propyl}$, demonstrate similar excitation and intense blue emission spectra. Other aliphatic substituents are expected to have similar properties. The inventors have further demonstrated that the excitation and emission spectra of $\text{Al}(\text{OR})_2(\text{dpa})$ where R is an aryl group such as phenyl are similar to Figure 1, and that the excitation and emission spectra of $\text{Al}_2(\text{OR})_4(\text{azain})_2$ where R is an aryl group such as phenyl are similar to Figure 2. The inventors have still further demonstrated electroluminescence of $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$, as is described in detail in Example 6 below.

The molecular structures of $\text{Al}(\text{CH}_3)_2(\text{dpa})$ and $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ have been determined by single-crystal X-ray diffraction analyses. Such analyses show that the dpa and the 7-azaindole ligands bind to the aluminum center either as a chelating ligand (the ligand binds to one aluminum center only) or as a bridging ligand (the ligand binds to two aluminum centers) (Figure 3-5). Apparently, the bond formation between the aluminum ion and the 7-azaindole or the dpa ligand is responsible for the high emission intensity of the blue luminescence produced by the complex.

Additional advantages provided by the compounds of the invention are improved stability and manageability for processing. In practical applications, it is often highly desirable for luminescent compounds to be processed to form high quality films. A superior way to achieve high quality films is by CVD, which requires the material to be thermally stable and sublimable under vacuum. Aluminum complexes as described herein demonstrate these desired properties. For example, the dimeric $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ compound is thermally stable up to 300 °C and can be sublimed at 0.07 mm Hg and 200 °C.

The $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ compound can degrade slowly upon exposure to air, due to the reaction of the methyl group with moisture, but we have found ways to overcome this problem. For instance, since the luminescence does not depend on the methyl groups, they can be replaced with more inert alkoxyl groups without destroying the luminescence. This can be achieved either by reacting 7-azaindole with $\text{Al}(\text{OR})_3$ directly or by reacting $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ with four equivalent HOR to form the $[\text{Al}(\text{OR})_2(\text{azain})]_2$ compound. The inventors have shown that the analogous alkoxyl compounds $\text{Al}(\text{OPr}^i)_2(\text{dpa})$ and $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$ can, like the alkyl compounds, be sublimed readily.

The volatility of a compound of the invention can be modified by modifying the R group: in general, the bulkier the R group, the more sublimable the compound, due to the

decreased attractive intermolecular interactions in the crystal lattice. It is possible to replace some of the methyl groups with hydroxyl (OH^-) or oxygen (O^{2-}) ligand by introducing moisture into the reaction medium. For example, $\text{Al}(\text{CH}_3)_3$ reacts with dpa in the presence of 0.5 equivalent H_2O to form the tetranuclear complex $\text{Al}_2(\text{CH}_3)_6(\text{O})_2(\text{dpa})_2$ (Figure 5), which is much more stable than $\text{Al}(\text{CH}_3)_2(\text{dpa})$ toward air and emits intense blue light as well.

Yet a further advantage of luminescent compounds of the invention is that they are highly soluble in common organic solvents such as toluene, diethyl ether, tetrahydrofuran (THF) and dichloromethane. This permits the compounds to be blended easily and conveniently with organic polymers. The role of the organic polymer in such a mixture is at least two-fold: First, a polymer can provide protection for the luminescent compound from air degradation. Second, a polymer host matrix permits the use of a spin-coating or dip-coating process as an alternative way to make luminescent films. Although spin-coating and dip-coating processes may not produce as high quality films as those produced by CVD, they are often much faster and more economical than CVD.

As an example of this application, the $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ compound forms a clear transparent solution with the non-luminescent polymer poly[1-(methoxycarbonyl)-1-methylethylene (poly(methyl methacrylate)) in toluene. This can be converted to a transparent film by evaporating the toluene solvent via either a dip-coating or spin-coating process. Films obtained in this way are stable in air for days without losing the intense blue luminescence (Figure 6). Certain polymers are expected to further enhance the luminescence of the emitter in the film.

In some embodiments of the invention, we have replaced the aluminum ion with boron, to further enhance the stability of the coordination complex. B-C, B-N, and B-O bonds in general are more covalent in nature than the corresponding aluminum bonds, and are therefore less susceptible to degradation by air and moisture. In addition, boron compounds have less tendency to form aggregates or oligomers, and are therefore generally more volatile than corresponding aluminum compounds. For example, $\text{B}(\text{dpa})\text{X}_2$, where X is halide or alkoxyl, has been found to produce blue luminescence, is stable in air and is sublimable. Specific examples of blue luminescent boron coordination complexes according to the invention are described in Examples 10 and 11 below.

The invention provides a method of producing electroluminescence comprising the steps of: providing an electroluminescent compound of the invention having a formula as set

out above (or a derivative thereof); and applying a voltage across said electroluminescent compound so that the compound electroluminesces.

According to the invention, electroluminescent devices for use with an applied voltage are provided. In general, such a device has a first electrode, an emitter which is an electroluminescent compound of the invention, and a second, transparent electrode, wherein a voltage is applied between the two electrodes to produce an electric field across the emitter of sufficient strength to cause the emitter to electroluminesce. Preferably, the first electrode is of a metal, such as, for example, aluminum, which reflects light emitted by the compound; whereas the second, transparent electrode permits passage of emitted light therethrough. The transparent electrode is preferably of indium tin oxide (ITO) glass or an equivalent known in the art. Here, the first electrode is the cathode and the second electrode is the anode.

Referring to Figure 29, a preferred embodiment of an electroluminescent device of the invention is shown. The emitter is interposed between an electron transport layer (e.g., Alq, BND, TAZ) adjacent the metal first electrode and a hole transport layer (e.g., TPD, α -NPD, mTADATA) adjacent the second, transparent electrode. The choice of the materials employed as hole and electron transport layers will depend upon the specific properties of the particular emitter employed. The hole or electron transport layer may also function as a supporting layer. The device is connected to a voltage source such that an electric field of sufficient strength is applied across the emitter. Blue light consequently emitted from the compound of the invention passes through the transparent electrode.

In some embodiments of the invention, the device includes one or more dielectric layers interposed between the emitter and one or both of the electrodes. Such dielectric layer(s) are employed in prior art systems with inorganic salt emitters to reduce the voltage drop across the emitter. In a first example of such a device, layers are arranged in a sandwich in the following order: first electrode, dielectric layer, emitter, and second, transparent electrode. In a preferred embodiment of this type, a substrate of glass, quartz or the like is employed. A reflective metal layer (corresponding to the first electrode) is deposited on one side of the substrate, and an insulating dielectric layer is deposited on the other side. The emitter layer which is a compound of the invention is deposited on the dielectric layer, preferably by CVD, though other methods may be equally effective. A transparent conducting ITO is then deposited on the emitter layer. An effective voltage is applied to produce electroluminescence of the emitter.

In a second example of an EL device of the invention a second dielectric layer is employed, the sandwich layers are arranged in the following order: first electrode, first dielectric layer, emitter, second dielectric layer and second, transparent electrode.

Electroluminescent devices of the invention may include one or more of the blue-emitting compounds described herein. Such devices may be flat panel display devices. In some embodiments of the invention, an electroluminescent device such as a flat panel display device may include not only a blue-emitting phosphor as described herein, but may be a multiple-color display device including one or more other phosphors. The other phosphors may emit in other light ranges, i.e., red, green, and/or be "stacked" relative to each other. Convenient materials, structures and uses of electroluminescent display devices are described in P.D. Rack *et al.*, *MRS Bulletin*, pp. 49-58 (March 1996).

All scientific and patent publications cited herein are hereby incorporated in their entirety by reference.

EXAMPLES

Example 1: Synthesis of $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$

0.50 mmol of 7-azaindole was dissolved in 10 mL of toluene under nitrogen. 0.50 mmol $\text{Al}(\text{CH}_3)_3$ (0.25 mL of 2 M $\text{Al}(\text{CH}_3)_3$ solution in hexane) was added to the solution at 23 °C. The mixture was stirred for 1.5 h. The solution was concentrated to about 5 mL. The product $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$ was isolated as colorless crystals, at 60% yield.

Example 2: Synthesis of $\text{Al}(\text{CH}_3)_2(\text{dpa})$

0.50 mmol of di-2-pyridyl amine was dissolved in 10 mL of toluene under nitrogen. 0.5 mmol $\text{Al}(\text{CH}_3)_3$ (0.25 mL of 2 M $\text{Al}(\text{CH}_3)_3$ solution in hexane) was added to the solution at 23 °C. The mixture was stirred for 3.0 h. The solution was concentrated to about 5 mL. The product $\text{Al}(\text{CH}_3)_2(\text{dpa})$ was isolated as colorless crystals, at > 60% yield.

Example 3: Synthesis of $[\text{Al}_2(\text{CH}_3)_3\text{O}(\text{dpa})]_2$

1 mmol of di-2-pyridyl amine was dissolved in 10 mL of toluene under nitrogen. 0.5 mmol $\text{Al}(\text{CH}_3)_3$ (0.25 mL of 2 M $\text{Al}(\text{CH}_3)_3$ solution in hexane) was added to the solution at 23 °C. 0.25 mmol of H_2O in toluene was added. The mixture was stirred for 3.0 h. The solution was concentrated to about 5 mL. The product $[\text{Al}_2(\text{CH}_3)_3\text{O}(\text{dpa})]_2$ was isolated as

colorless crystals, at > 50% yield.

Example 4: Synthesis of $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$

0.5 mmol of 7-azaindole was dissolved in 15 mL of toluene under nitrogen. 0.50
5 mmol $\text{Al}(\text{OPr}^i)_3$ was added to the solution at 23 °C. The mixture was stirred 0.5 h at 23 °C
and 0.5 h at 80 °C. The solution was evaporated to dryness in vacuum. The colorless powder
product $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$ was purified by sublimation at 80 °C and 0.04 mmHg.

Example 5: Synthesis of $\text{Al}(\text{OPr}^i)_2(\text{dpa})$

10 Compound $\text{Al}(\text{OPr}^i)_2(\text{dpa})$ was prepared by the same procedure as $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$
except that 7-azaindole was replaced by di-2-pyridyl amine.

Example 6: Electroluminescence of $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$

Electroluminescence of $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$ was demonstrated using the shadow mask
15 technique described in X. Yu and M. Sayer, "Thin film electroluminescent displays", *J. Can.*
Ceram. Soc. 55: 1 (1986), the contents of which are hereby incorporated by reference.

According to one embodiment of this technique, two electrodes are provided that are,
respectively, a first set of parallel lines applied using a shadow mask, and a second set of
parallel lines perpendicular to the first set that are also applied using a shadow mask. A layer
20 of test sample is interposed between the two electrodes, and an electric field is thereby
applied to the sample.

A sample of 200 mg of $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$ was dissolved in 3 mL of CH_2Cl_2 at 23 °C.
The resulting solution was spin-coated onto indium tin oxide (ITO) coated glass having a first
electrode in the form of an etched shadow mask pattern of parallel lines spaced 1 mm apart.

25 The sample film so-produced was approximately 2 in x 1.5 in with a thickness of 2-4 μm . A
second, aluminum electrode layer was patterned onto the surface of the $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$
film by metal evaporation through a shadow mask of parallel lines spaced 1 mm apart and
perpendicular to the first set. (Thus, individual elements were 1 mm x 1 mm x 2-4 μm in
size.) Silver paste was used to contact the ITO layer. Blue luminescence was observed at an
30 applied voltage of approximately 50 V AC at 60 Hz and an injection current of 200-500 mA.
In preferred embodiments of the invention, electroluminescence is improved by using higher
quality films and/or a multiple layer device.

Example 7: Synthesis of $\text{Al}_2(\text{CH}_3)_2(\text{azain})_4$

200 mg (1.70 mmol) of 7-azaindole in 8 mL of toluene was reacted with 423 mL (0.846 mmol) of $\text{Al}(\text{CH}_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen. The reaction mixture was stirred for 3 h. The volume of the solution was reduced to approximate 2 mL by vacuum. 2 mL of hexane was added to crystallize the product. After a few days standing at 23 °C, colorless crystals of compound $\text{Al}_2(\text{CH}_3)_2(\text{azain})_4$ were obtained in 62% yield. When excited by UV light ($\lambda = 397 \text{ nm}$), this compound emits blue color at ($\lambda_{\text{max}} = 442 \text{ nm}$ (Figure 8). The structure of compound $\text{Al}_2(\text{CH}_3)_2(\text{azain})_4$ was determined by single-crystal X-ray diffraction analysis. There are four bridging 7-azaindole ligands in $\text{Al}_2(\text{CH}_3)_2(\text{azain})_4$, as shown in Figure 9.

Example 8: Synthesis of $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$

Compound $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$ is an example of stable aluminum complexes where the reactive methyl groups are replaced by alkoxy groups.

$\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$ was obtained by the following procedure: 200 mg (1.70 mmol) of 7-azaindole in 8 mL of toluene was reacted with 847 mL (1.70 mmol) of $\text{Al}(\text{CH}_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen for 1 h. 386 mg (2.30 mmol) of hexafluoro-2-propanol in 2 mL of toluene was added to the reaction mixture. This mixture was stirred for additional 3 h at 23 °C. The volume of the solution was then concentrated to about 2 mL by vacuum. After several days standing at 23 °C, colorless crystals of $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$ were obtained in 65% yield. Compound $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$ has a blue emission band at $\lambda_{\text{max}} = 430 \text{ nm}$ (Figure 10). Its structure was determined by single-crystal X-ray diffraction analysis. $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$ contains two chemically non-equivalent aluminum environments. One of the aluminum atoms is coordinated by two hexafluoro-2-propanolato ligands and the other is coordinated by a methyl ligand. There is a bridging hexafluoro-2-propanolato ligand and two bridging 7-azaindole ligands in the molecule (Figure 11).

Example 9: Synthesis of $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$

Compound $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$ is the second example of alkoxy or oxo ligand-stabilized aluminum compounds. It was obtained by the following procedure: 200 mg (1.70 mmol) of 7-azaindole in 7 mL of toluene was reacted with 423 mL (0.846 mmol) of

$\text{Al}(\text{CH}_3)_3$ (2.0 M in hexane) at 23 °C under nitrogen for 3 h. 142 mg of hexafluoro-2-propanol (0.846 mmol) in 3 mL of toluene was added. The mixture was stirred for another 3 h and concentrated to about 2 mL by vacuum. 2 mL of THF and 1 mL of hexane were added to the solution to crystallize the product. After two days, colorless crystals of

5 $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$ were obtained in 62% yield. Compound $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$ has a blue emission band at $\lambda_{\text{max}} = 430$ nm (Figure 12). Its crystal structure was determined by X-ray diffraction analysis.

$\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$ has three aluminum ions linked by a triply bridging oxygen atom. There are four bridging 7-azaindole ligands in the molecule. The two alkoxy

10 ligands function as monodentate ligands (Figure 13).

Example 10: Synthesis of $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$

Blue luminescent compound $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$ was made according to the following procedure: 200 mg (1.70 mmol) of 7-azaindole in 7 mL toluene was reacted with

15 1.70 mL (1.70 mmol) of $\text{B}(\text{C}_2\text{H}_5)_3$ (1.0 M in hexane) under nitrogen. This mixture was refluxed for 4 h under nitrogen. After the concentration of the solution, colorless crystals of $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$ were obtained in 46% yield. Compound $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$ has a blue emission band at $\lambda_{\text{max}} = 397$ nm (Figure 14). Its crystal structure has been determined by X-ray diffraction analysis. Two 7-azaindole ligands, a neutral one and a

20 deprotonated one, are bound to the boron center (Figure 15).

Example 11: Synthesis of $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$

Compound $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$ has been demonstrated to be a stable blue luminescent boron compound. This compound was obtained by the following procedure:

25 500 mg (4.23 mmol) of 7-azaindole in 20 mL of toluene was reacted with 4.23 mL (4.23 mmol) of $\text{B}(\text{C}_2\text{H}_5)_3$ (1.0 M in hexane) under nitrogen at 23 °C. After the mixture was stirred for 3 h, 3 drops of water were added to the solution via a pipette. The reaction mixture was stirred for another 4 h. It was then concentrated to a volume of 3 mL. 2 mL of hexane was added to crystallize the product. Colorless crystals of $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$ formed after

30 about 24 h at 23 °C. Compound $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$ has a blue emission band at $\lambda_{\text{max}} = 422$ nm (Figure 16). Both blue photoluminescence and blue electroluminescence have been demonstrated. The structure of $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$ was determined by X-ray diffraction

analysis. It contains two boron atoms linked by an oxygen atom. The two boron centers are also bound by two 7-azaindole ligands (Figure 17). This compound is remarkably stable towards air and moisture. It melts at 290 °C without decomposition. It can be sublimed at about 150 °C and 0.06 torr.

Example 12: Synthesis of 2-phenyl-7-azaindole

The synthetic procedure of R. Herbert and D. G. Wibberley, *J. Chemical Society, C*, 1505 (1969), was employed, with minor modifications.

2-phenyl-7-azaindole was prepared in two steps. First, 2-amino-3-picoline was reacted with benzoyl chloride in chloroform in the presence of pyridine to produce 2-benzamido-3-picoline in 33% yield. Second, pyrolysis of 2-benzamido-3-picoline in N-methylaniline in the presence of NaH at 280°C was performed to produce 2-phenyl-7-azaindole (Figure 18) in 58% yield. This compound was characterized by NMR spectroscopy.

Example 13: Synthesis of 2-methyl-7-azaindole

The synthetic procedure of R. Herbert and D. G. Wibberley, *J. Chemical Society, C*, 1505 (1969), was employed, with minor modifications.

2-methyl-7-azaindole was prepared in two steps. First, 2-amino-3-picoline was reacted with acetyl chloride in toluene in the presence of pyridine to produce 2-acetamido-3-picoline in 65% yield. Second, pyrolysis of 2-acetamido-3-picoline in N-methylaniline in the presence of NaH at 280°C was performed to produce 2-methyl-7-azaindole (Figure 18) in 23% yield. This compound was characterized by NMR spectroscopy.

Example 14: Synthesis of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{Ph-azain})_4$

2-Phenyl-7-azaindole (0.078 g, 0.40 mmol) in 10 mL toluene was heated to 60°C. After all of the 2-phenyl-7-azaindole was dissolved in the toluene, $\text{Al}(\text{CH}_3)_3$ (0.15 mL, 2M, 0.3 mmol) was added. The solution was stirred for 5 h at room temperature while water-saturated $\text{N}_2(\text{g})$ was passed through the reaction container. The solution was stirred for another 15 h. The mixture was concentrated to about 2 mL by vacuum. Colorless crystals of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{Ph-azain})_4$ (Figure 19) were obtained. Yield: 0.140 g (77%). This compound

has an emission maximum at $\lambda = 472$ nm and an excitation maximum, $\lambda = 375$ nm (Figure 20).

Example 15: Synthesis of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{CH}_3\text{-azain})_4$

2-Methyl-7-azaindole (0.159 g, 1.20 mmol) in 8.0 mL of toluene was reacted with $\text{Al}_3(\text{CH}_3)_3$ (0.45 mL, 2M, 0.90 mmol) and the solution was stirred for 5 h at room temperature. Water-saturated nitrogen gas was passed through the reaction container. After the solution was stirred for another 15 h, it was concentrated to about 2 mL by vacuum. Colorless crystals of $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{CH}_3\text{-azain})_4$ (Figure 21) were obtained. Yield: 0.142 g (71%). This compound has an emission maximum at $\lambda=425$ nm (Figure 22).

Example 16: Synthesis of pentafluorophenyl-2-pyridylamine

This compound was synthesized according to the method of R. Koppang, *J. Organometallic Chemistry*, 46, 193 (1972). Lithium (2-pyridyl)amide was obtained from the reaction of lithium amide with 2-aminopyridine in a 1:1 ratio in THF. The reaction of lithium (2-pyridyl)amide with hexafluorobenzene in THF at 0°C yielded pentafluorophenyl-2-pyridylamine (PFPA-H; 2-pentafluoroanilinopyridine) (Figure 23) in 76% yield. The product was characterized by NMR spectroscopy.

Example 17: Synthesis of $\text{Al}(\text{PFPA})_3$

Pentafluorophenyl-2-pyridylamine (0.156 g, 0.60 mmol) in 5 mL of toluene was reacted with $\text{Al}(\text{CH}_3)_3$ (0.10 mL 2.0 M in hexane, 0.20 mmol) at room temperature under nitrogen for 12 h. The mixture was concentrated to about 1 mL by vacuum. Colorless crystals of $\text{Al}(\text{PFPA})_3$ (Figure 24) were obtained. Yield: 0.126 g (78%). This compound has an emission maximum at $\lambda=401$ nm when excited at $\lambda=344$ nm (Figure 25).

Example 18: Synthesis of $\text{B}(\text{Ph})_3(\text{azainH})$

Triphenylborane (1.211 g, 5 mmol) in 20 mL toluene was reacted with 7-azaindole (0.592 g, 5 mmol) for 5 h. The solvent was removed by vacuum. The solid was transferred to a drybox and re-dissolved in a minimum volume of CH_2Cl_2 . After the addition of 2-3 mL of hexane, colorless crystals of $\text{B}(\text{Ph})_3(\text{azainH})$ (Figure 26) were obtained. Yield: 1.18 g (65%). This compound has an emission maximum at a $\lambda = 434$ nm (Figure 27).

Example 19: Synthesis of B(OPh)₃(azainH)

Triphenylborate (0.870 g, 3 mmol) in 20 mL toluene was reacted with 7-azaindole (0.354 g, 3 mmol) for 5 h. The solvent was removed by vacuum. The solid was transferred to a drybox and re-dissolved in a minimum volume of CH₂Cl₂. After the addition of 2 mL
5 hexane, colorless crystals of B(OPh)₃(azainH) were obtained. Yield: 0.865 g (71%). This compound has an analogous crystal structure to that of B(Ph)₃(azainH) shown in Figure 26, and has an emission maximum at $\lambda = 430$ nm (Figure 28).

Although this invention is described in detail with reference to preferred embodiments
10 thereof, these embodiments are offered to illustrate but not to limit the invention. It is possible to make other embodiments that employ the principles of the invention and that fall within its spirit and scope as defined by the claims appended hereto.

WHAT IS CLAIMED IS:

1. A photoluminescent or electroluminescent compound having a formula selected from the group consisting of:

- (i) $[AlR_2(azain)]_n$,
- (ii) $[AlR_2(dpa)]_n$,
- (iii) $[Al_4R_6O_2(dpa)_2]$,
- (iv) $Al(PFPA)_3$, and
- (v) derivatives of (i), (ii), (iii), and (iv),

where R is aliphatic, aryl or alkoxyl, azain is deprotonated 7-azaindole, dpa is deprotonated di-2-pyridyl amine, and PFPA is deprotonated pentafluorophenyl-2-pyridylamine.

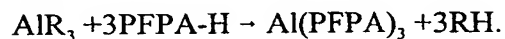
2. A method of synthesizing a compound as claimed in claim 1, comprising a step selected from the group consisting of:



where (n = 1 or 2);



and



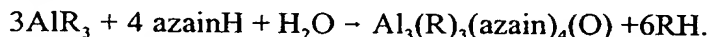
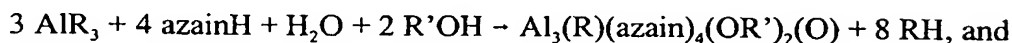
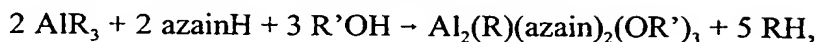
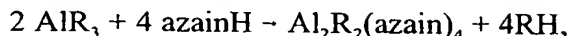
3. A photoluminescent or electroluminescent compound having a formula selected from the group consisting of:

- (i) $Al_2R_2(azain)_4$,
- (ii) $Al_2(R)(azain)_2(OR')_3$,
- (iii) $Al_3(R)(azain)_4(OR')_2(O)$,
- (iv) $Al_3R_3(azain)_4(O)$, and
- (v) derivatives of (i), (ii), (iii) and (iv),

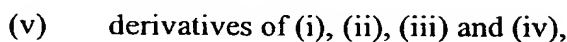
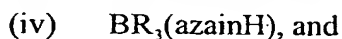
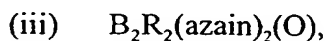
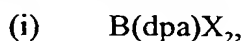
where R and R' are aliphatic, aryl or alkoxyl, azain is deprotonated 7-azaindole, and dpa is deprotonated di-2-pyridyl amine.

4. A method of synthesizing a compound as claimed in claim 3, comprising a step

selected from the group consisting of:

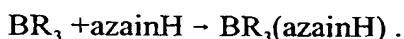
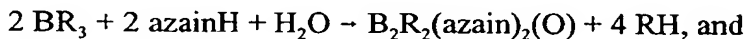
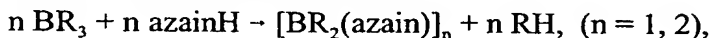


5. A photoluminescent or electroluminescent compound having a formula selected from the group consisting of:

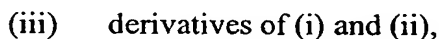
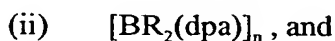


where azain is deprotonated 7-azaindole, dpa is deprotonated di-2-pyridyl amine, X is halide or alkoxyl, and R is aliphatic, aryl or alkoxyl.

6. A method of synthesizing a compound as claimed in claim 5, comprising a step selected from the group consisting of:



7. A photoluminescent or electroluminescent compound having a formula selected from the group consisting of:



where dpa is deprotonated di-2-pyridyl amine, and R and R' are aliphatic, aryl or alkoxy groups.

8. A method of synthesizing a compound as claimed in claim 7, comprising a step selected from the group consisting of:



9. A composition comprising a compound as claimed in claim 1, 3, 5 or 7 and an inert
5 carrier.

10. A composition comprising a compound as claimed in claim 1, 3, 5 or 7, an organic
polymer and a solvent.

10 11. A photoluminescent product or an electroluminescent product comprising a
compound as claimed in claim 1, 3, 5 or 7.

12. The product of claim 11, wherein the compound is applied by chemical vapor
deposition.

15 13. The product of claim 11, wherein the compound is applied by spin-coating or dip-
coating.

14. The product of claim 11, wherein the product is a flat panel display device.

20 15. The product of claim 11, wherein the product is a luminescent probe.

16. Use of a compound as claimed in claim 1, 3, 5 or 7 as a component of a
photoluminescent or electroluminescent product.

25 17. A method of producing electroluminescence, comprising the steps of:
providing an electroluminescent compound as claimed in claim 1, 3, 5 or 7, and
applying a voltage across said compound so that said compound electroluminesces.

30 18. An electroluminescent device for use with an applied voltage, comprising:
a first electrode,
an emitter which is an electroluminescent compound as claimed in claim 1, 3, 5 or 7,

and

a second, transparent electrode,
wherein voltage is applied between the two electrodes to produce an electric field
across the emitter so that the emitter electroluminesces.

5

19. An electroluminescent device for use with an applied voltage, comprising:
a first electrode,
a second, transparent electrode,
an electron transport layer adjacent the first electrode,
10 a hole transport layer adjacent the second electrode, and
an emitter which is an electroluminescent compound as claimed in claim 1, 3, 5 or 7
interposed between the electron transport layer and the hole transport layer ,
wherein voltage is applied between the two electrodes to produce an electric field
across the emitter so that the emitter electroluminesces.

15

20. $[\text{Al}(\text{CH}_3)_2(\text{azain})]_2$, where azain is deprotonated 7-azaindole.

21. $[\text{Al}(\text{OR})_2(\text{azain})]_2$, where R is aliphatic, aryl or alkoxyl, and azain is deprotonated 7-
azaindole.

20

22. $\text{Al}(\text{CH}_3)_2(\text{dpa})$, where dpa is deprotonated di-2-pyridyl amine.

23. $[\text{Al}(\text{OR})_2(\text{dpa})]_2$, where R is aliphatic, aryl or alkoxyl, and dpa is deprotonated di-2-
pyridyl amine.

25

24. $\text{Al}_2(\text{CH}_3)_6(\text{O})_2(\text{dpa})_2$, where dpa is deprotonated di-2-pyridyl amine.

25. $[\text{Al}(\text{OPr}^i)_2(\text{azain})]_2$, where azain is deprotonated 7-azaindole, and Pr^i is *iso*-propyl.

30

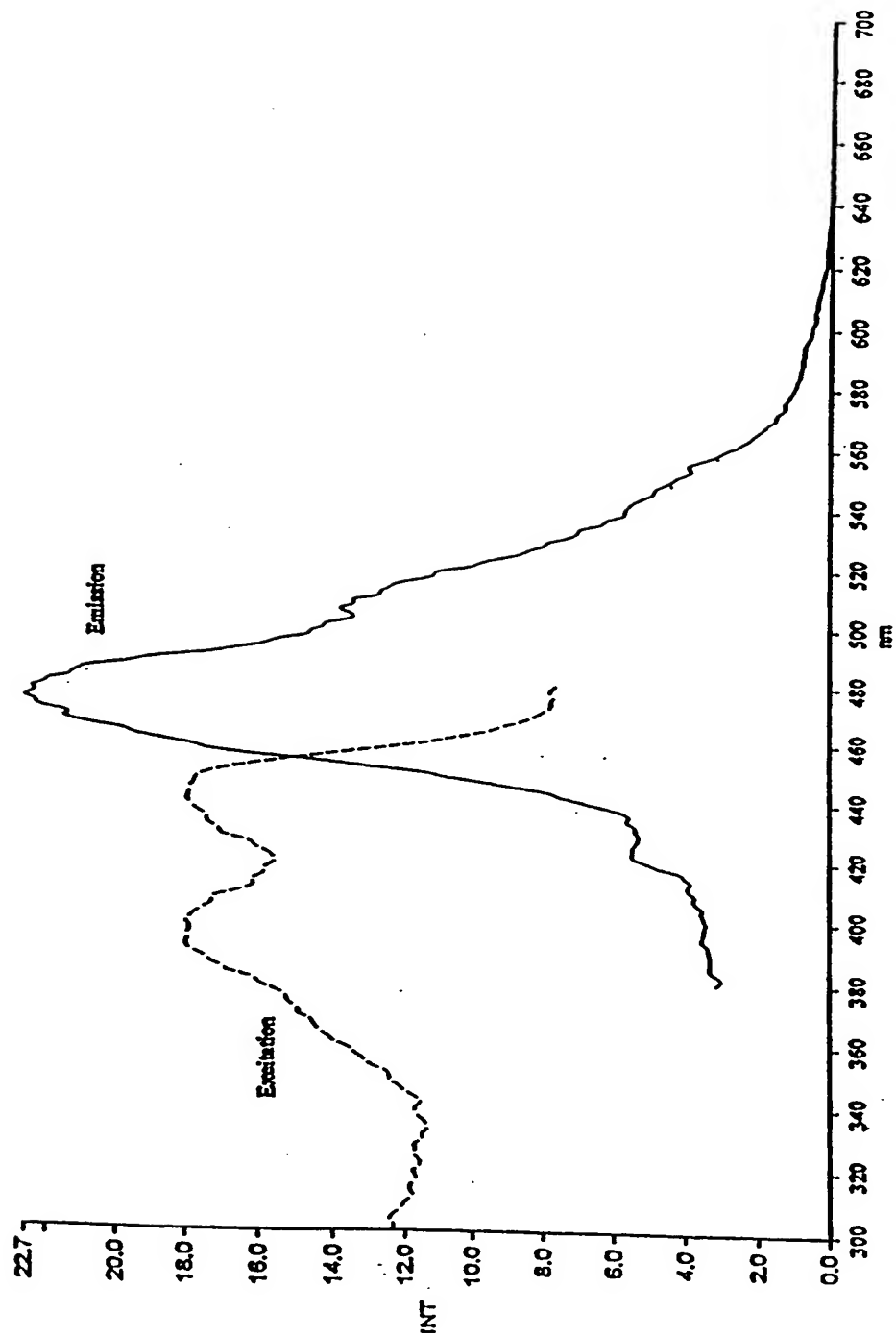
26. $\text{B}(\text{dpa})\text{X}_2$, where dpa is deprotonated di-2-pyridyl amine, and X is halide or alkoxyl.

27. $\text{Al}_2(\text{CH}_3)_2(\text{azain})_4$, where azain is deprotonated 7-azaindole.

28. $\text{Al}_2(\text{OCH}(\text{CF}_3)_2)_3(\text{azain})_2(\text{CH}_3)$, where azain is deprotonated 7-azaindole.
29. $\text{Al}_3(\text{OCH}(\text{CF}_3)_2)_2(\text{O})(\text{azain})_4(\text{CH}_3)$, where azain is deprotonated 7-azaindole.
- 5 30. $\text{B}(\text{C}_2\text{H}_5)_2(\text{azain})(\text{azainH})$, where azain is deprotonated 7-azaindole.
31. $\text{B}_2(\text{C}_2\text{H}_5)_2(\text{azain})_2(\text{O})$, where azain is deprotonated 7-azaindole.
32. $\text{Al}(\text{PFPA})_3$, where PFPA is deprotonated pentafluorophenyl-2-pyridylamine.
- 10 33. $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{Ph-azain})_4$, where Ph is phenyl and azain is deprotonated 7-azaindole.
34. $\text{Al}_3(\text{CH}_3)_3(\text{O})(\text{CH}_3\text{-azain})_4$, where azain is deprotonated 7-azaindole.
- 15 35. $\text{B}(\text{Ph})_3(\text{azainH})$, where Ph is phenyl and azain is deprotonated 7-azaindole.
36. $\text{B}(\text{OPh})_3(\text{azainH})$, where Ph is phenyl and azain is deprotonated 7-azaindole.

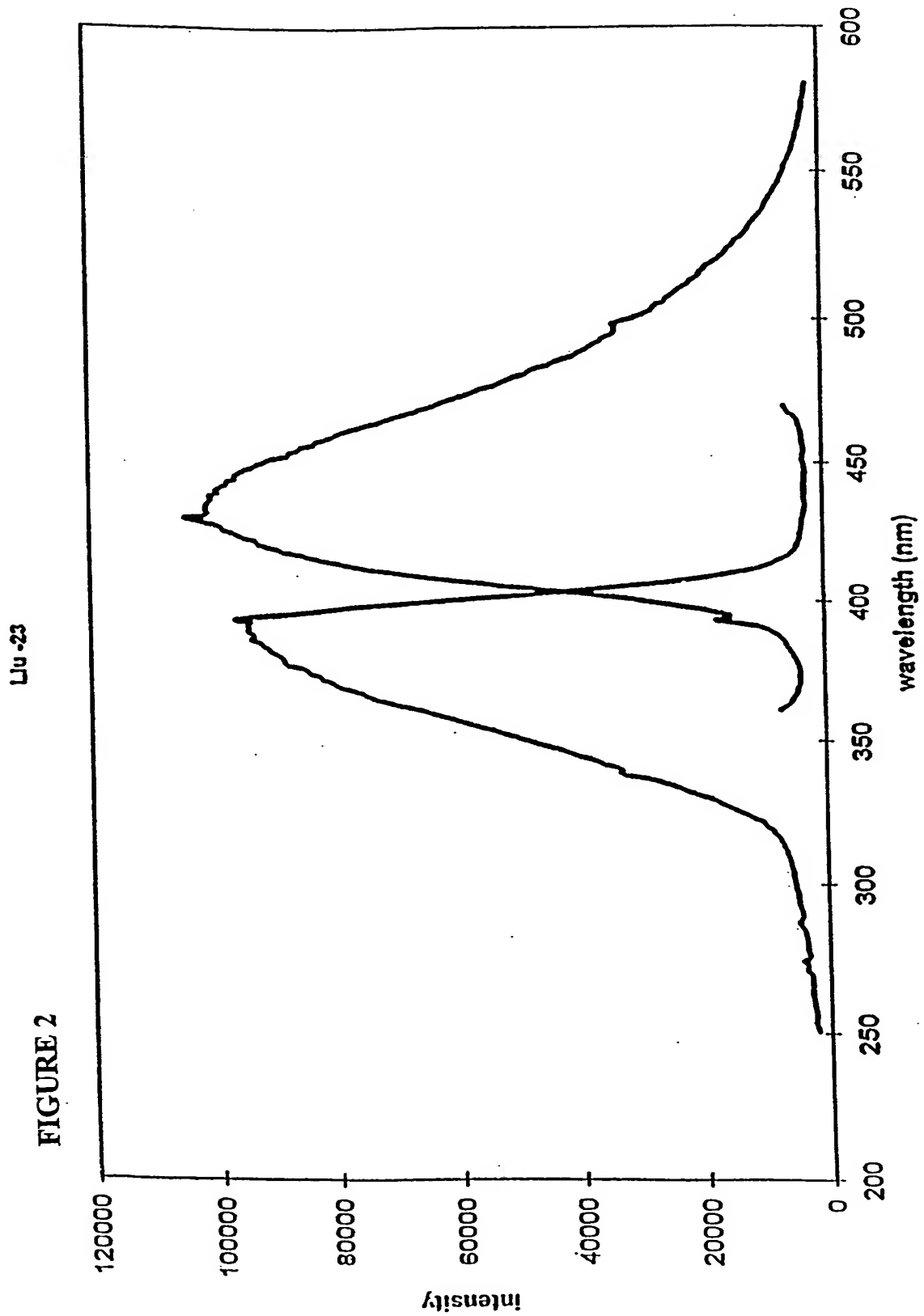
1/28

FIGURE 1



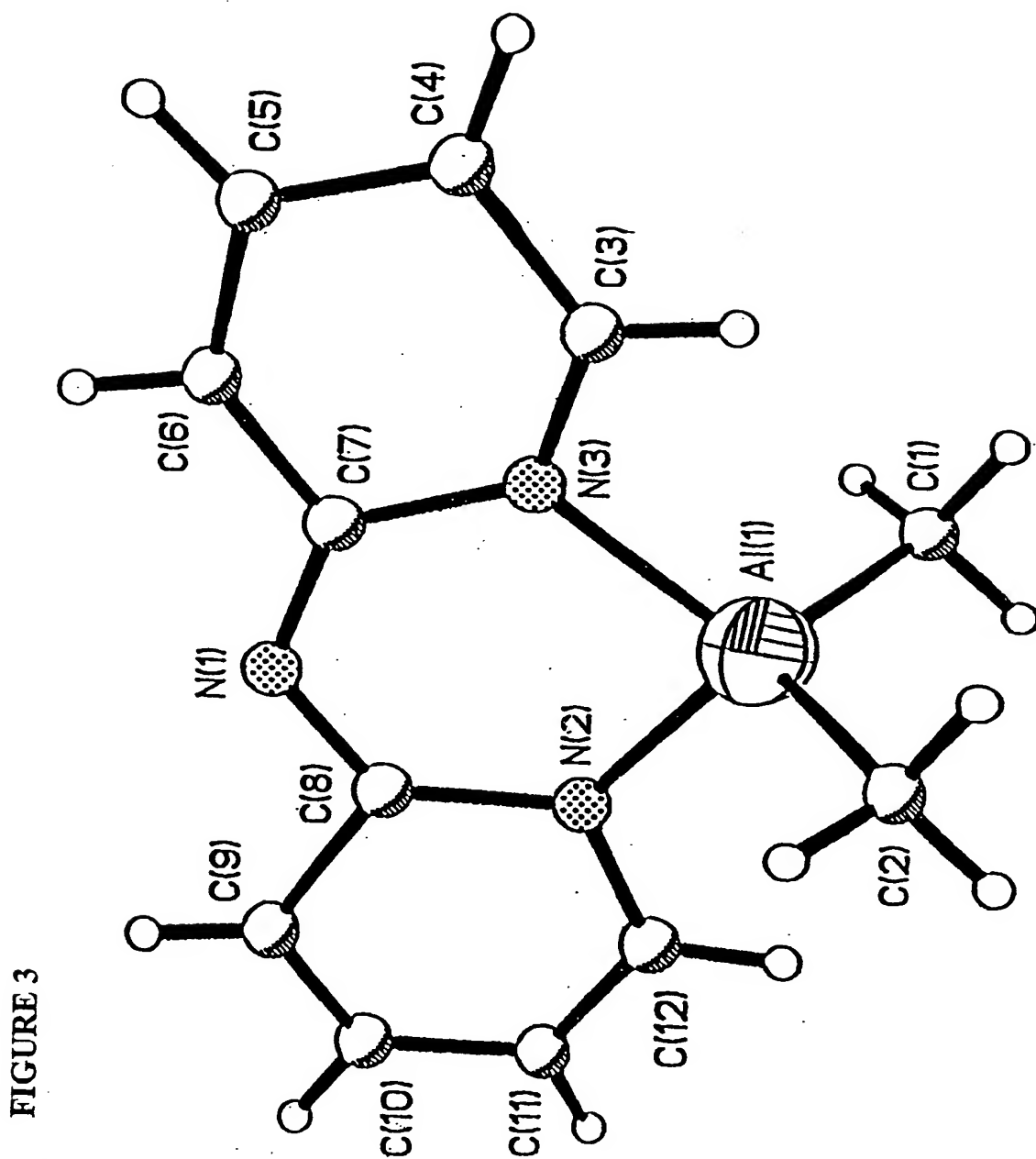
SUBSTITUTE SHEET (RULE 26)

2/28



SUBSTITUTE SHEET (RULE 26)

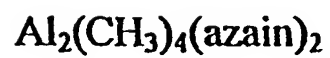
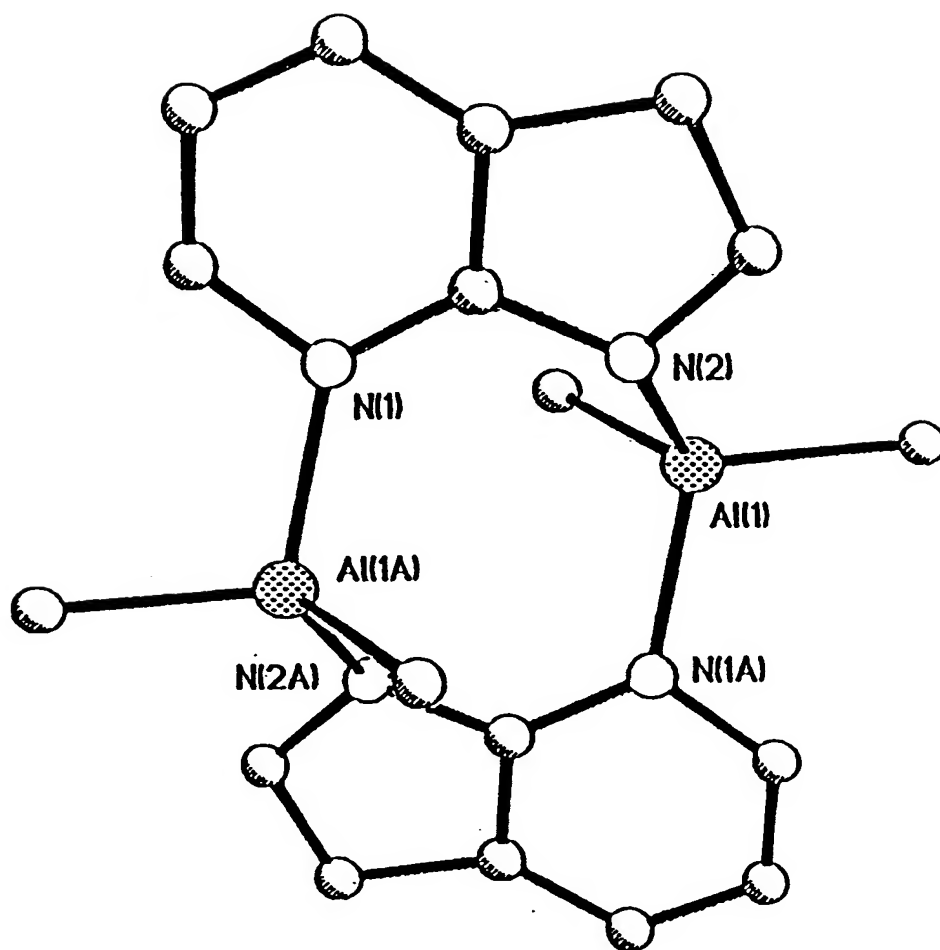
3/28



SUBSTITUTE SHEET (RULE 26)

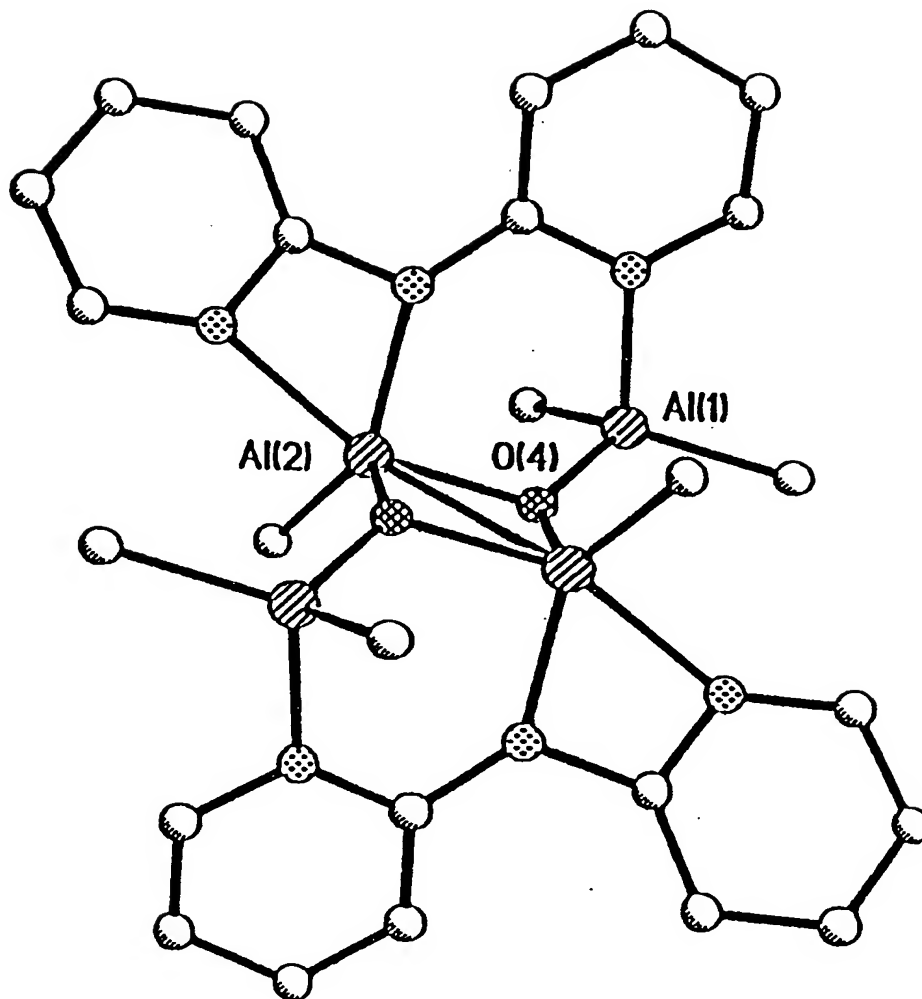
4/28

FIGURE 4



5/28

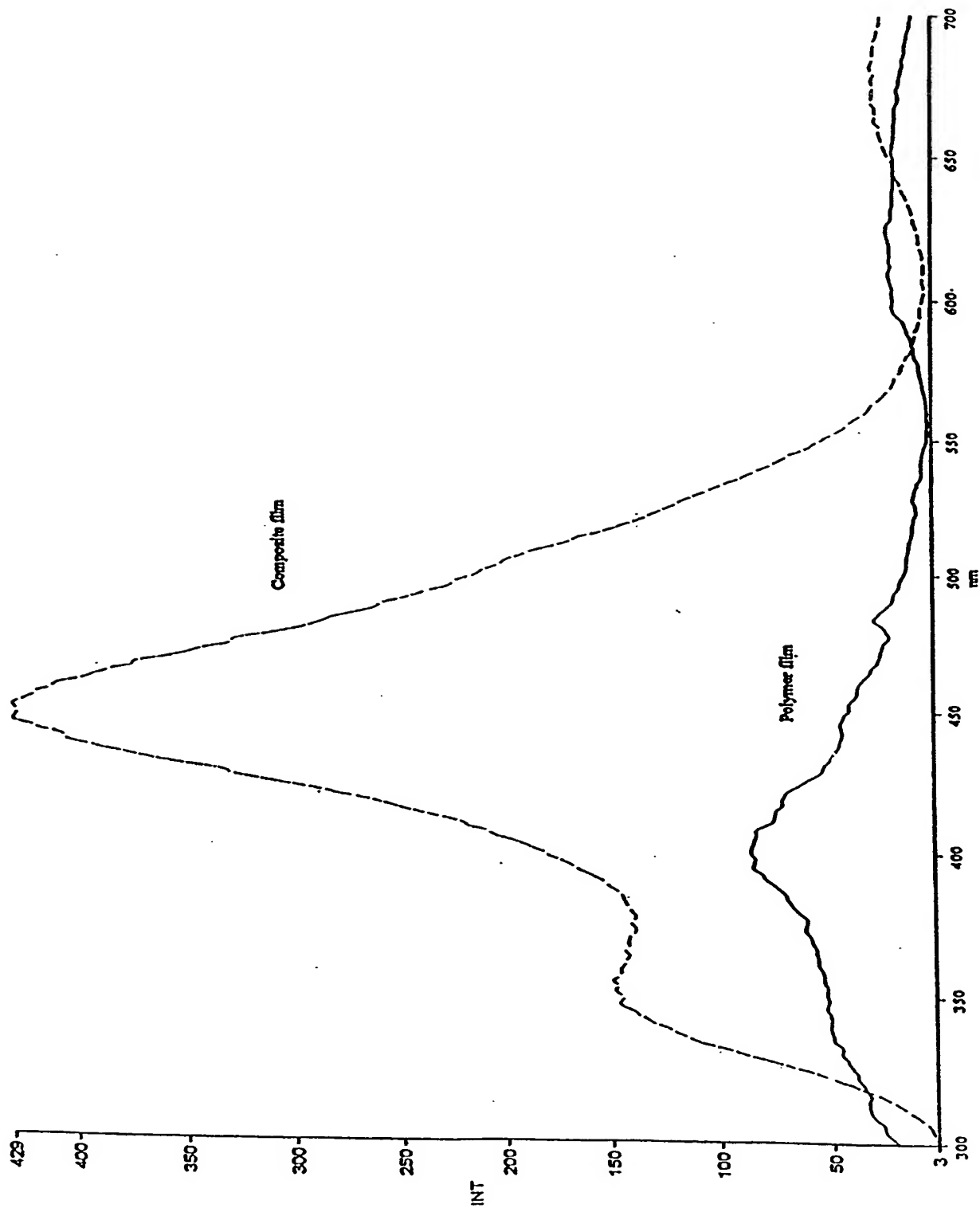
FIGURE 5



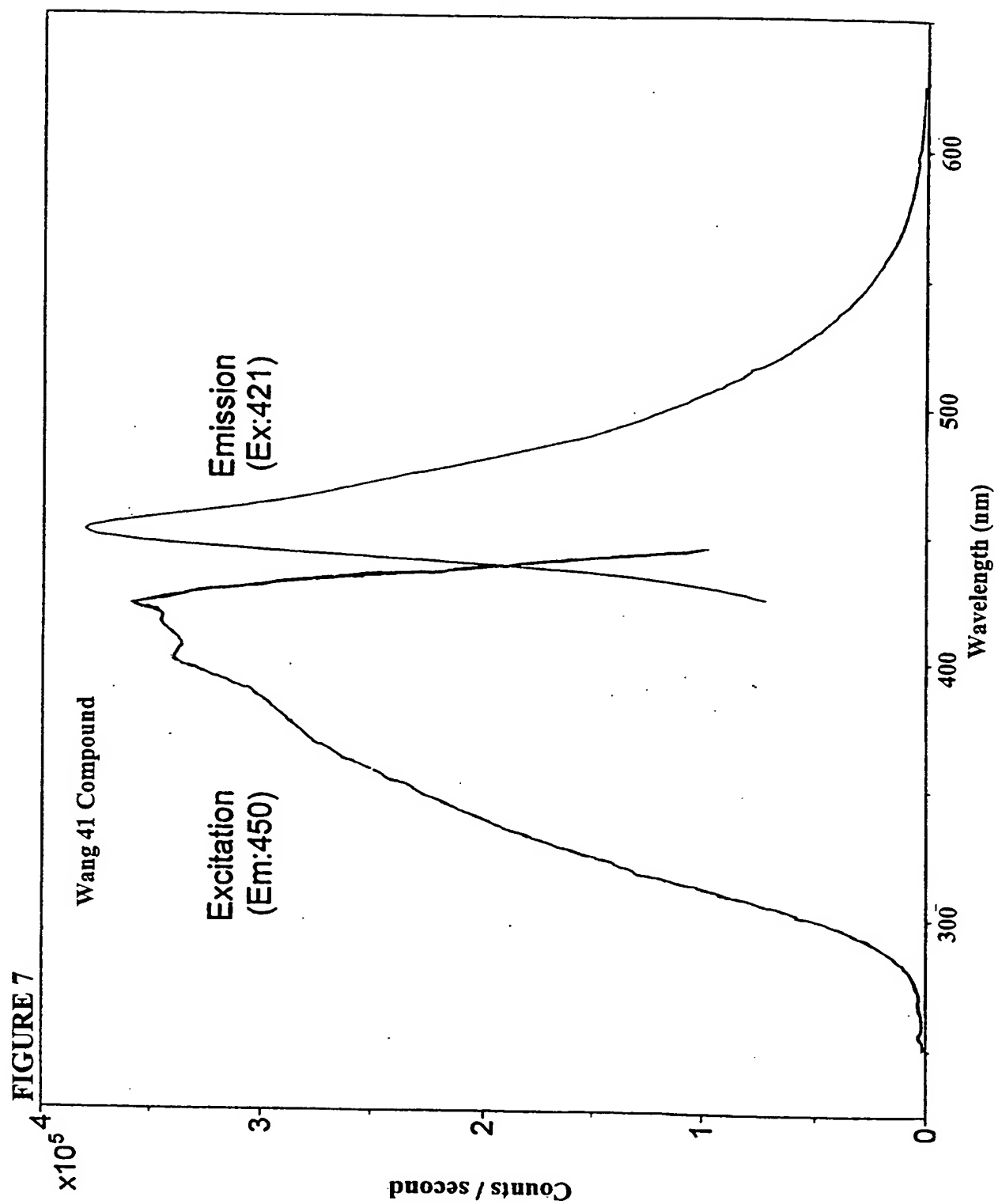
SUBSTITUTE SHEET (RULE 26)

6/28

FIGURE 6



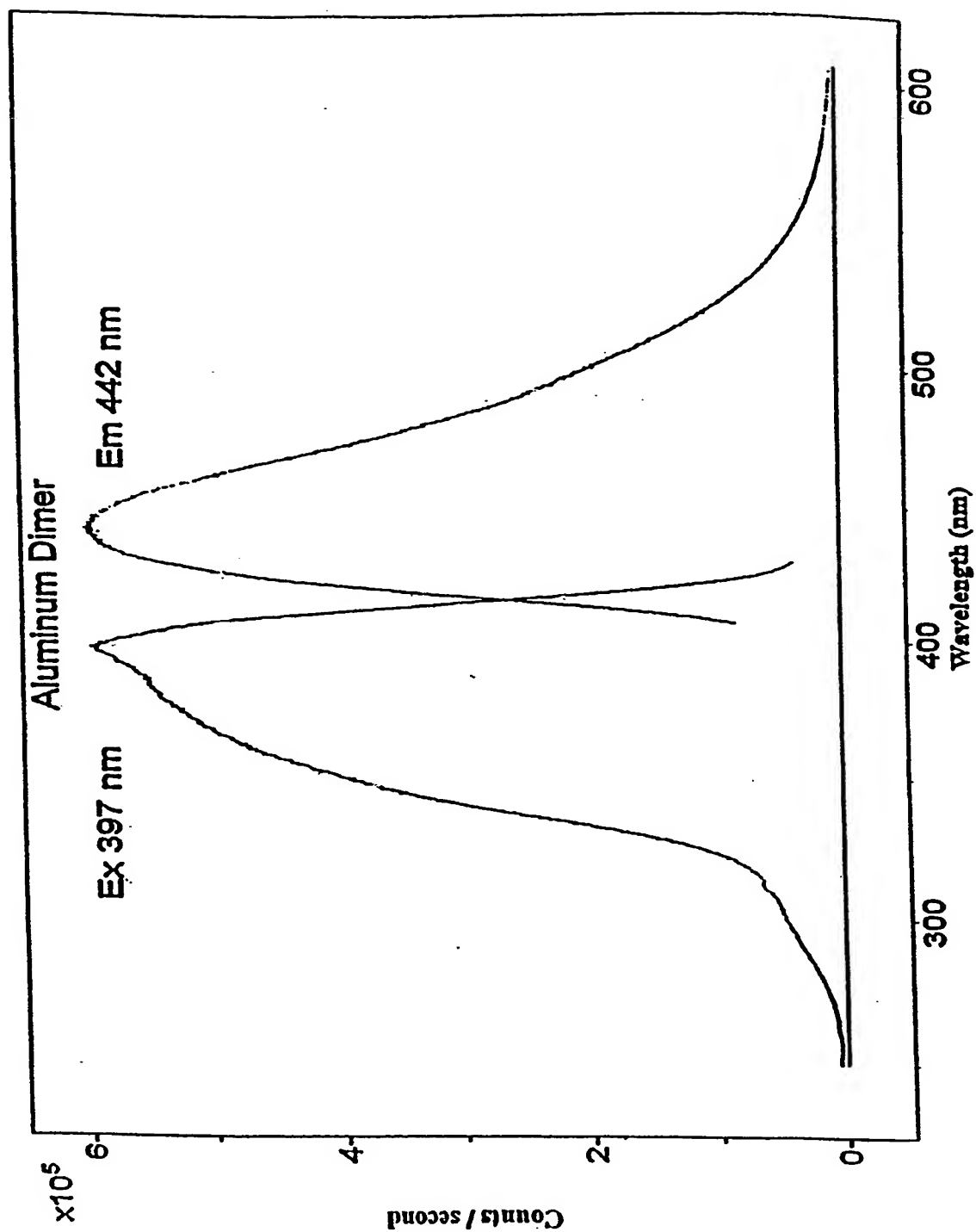
7/28



SUBSTITUTE SHEET (RULE 26)

8/28

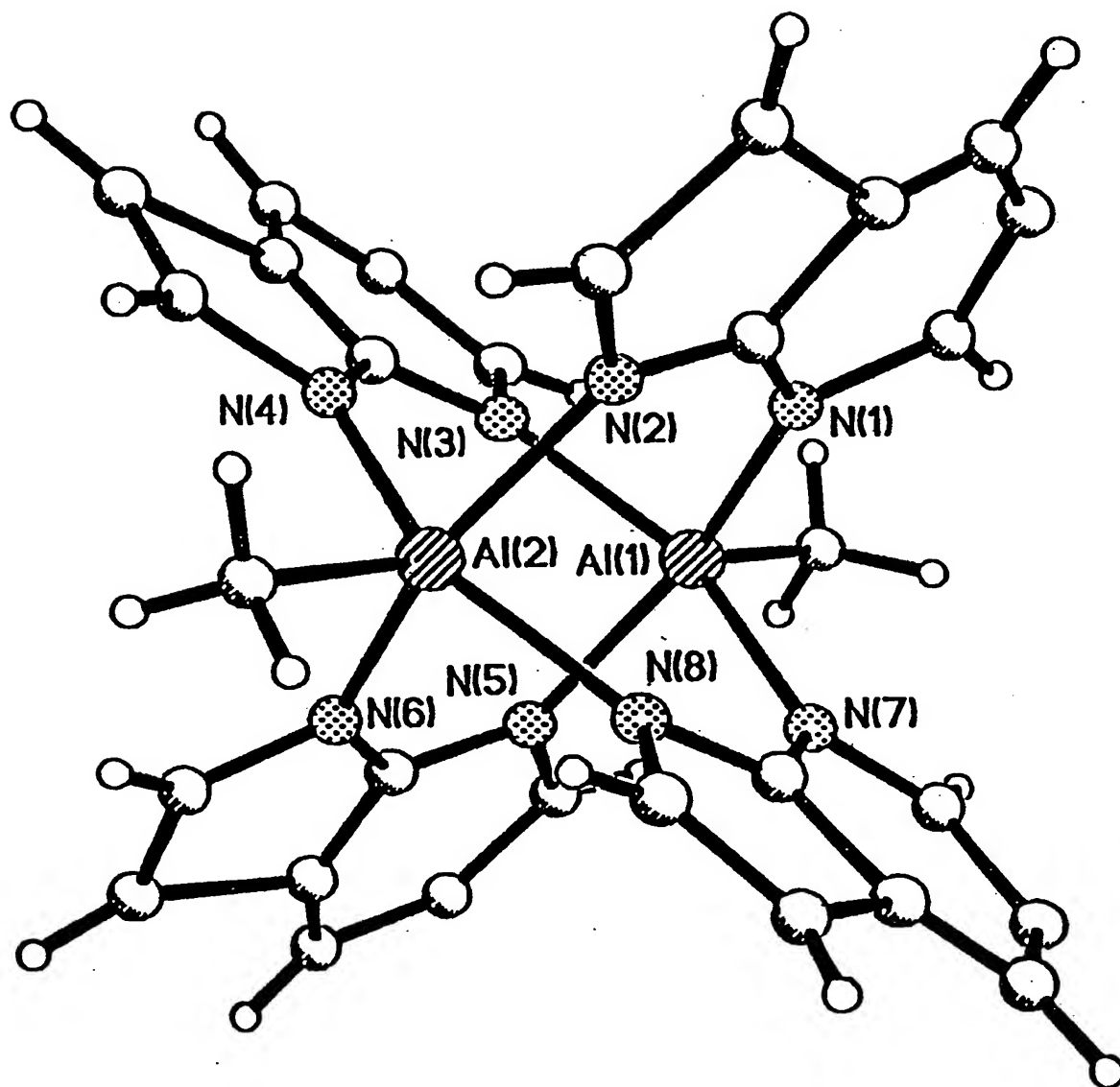
FIGURE 8



SUBSTITUTE SHEET (RULE 26)

9/28

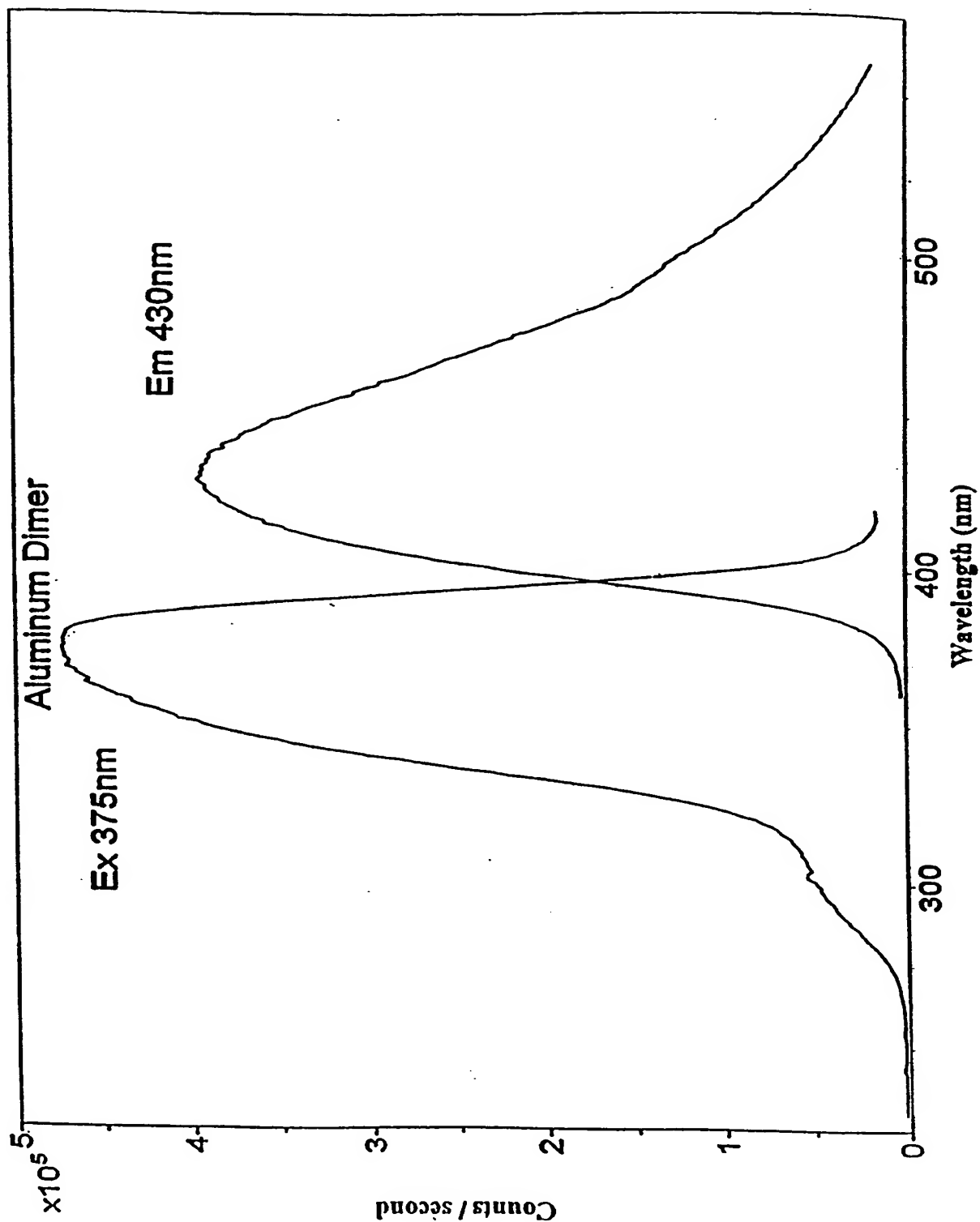
FIGURE 9



SUBSTITUTE SHEET (RULE 26)

10/28

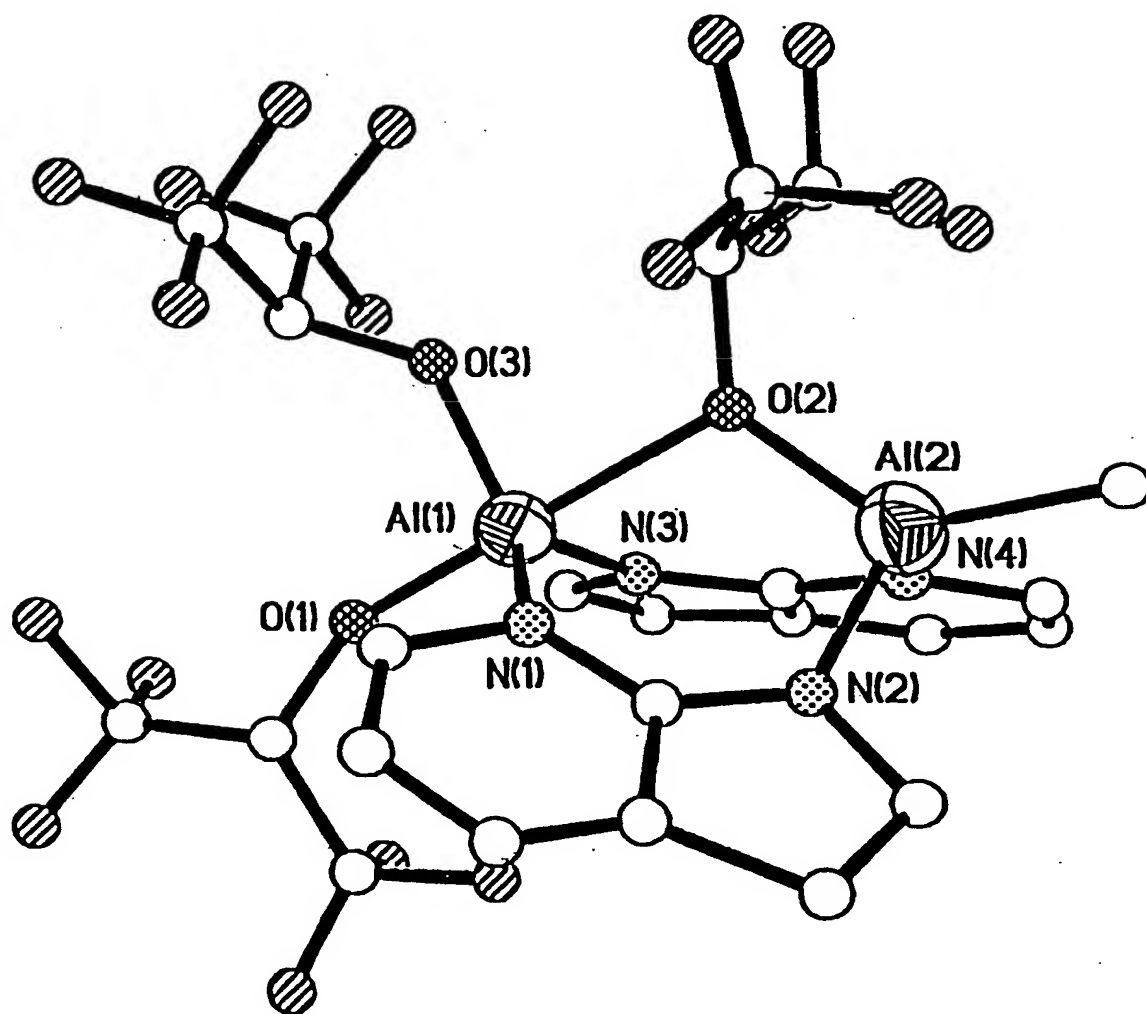
FIGURE 10



SUBSTITUTE SHEET (RULE 26)

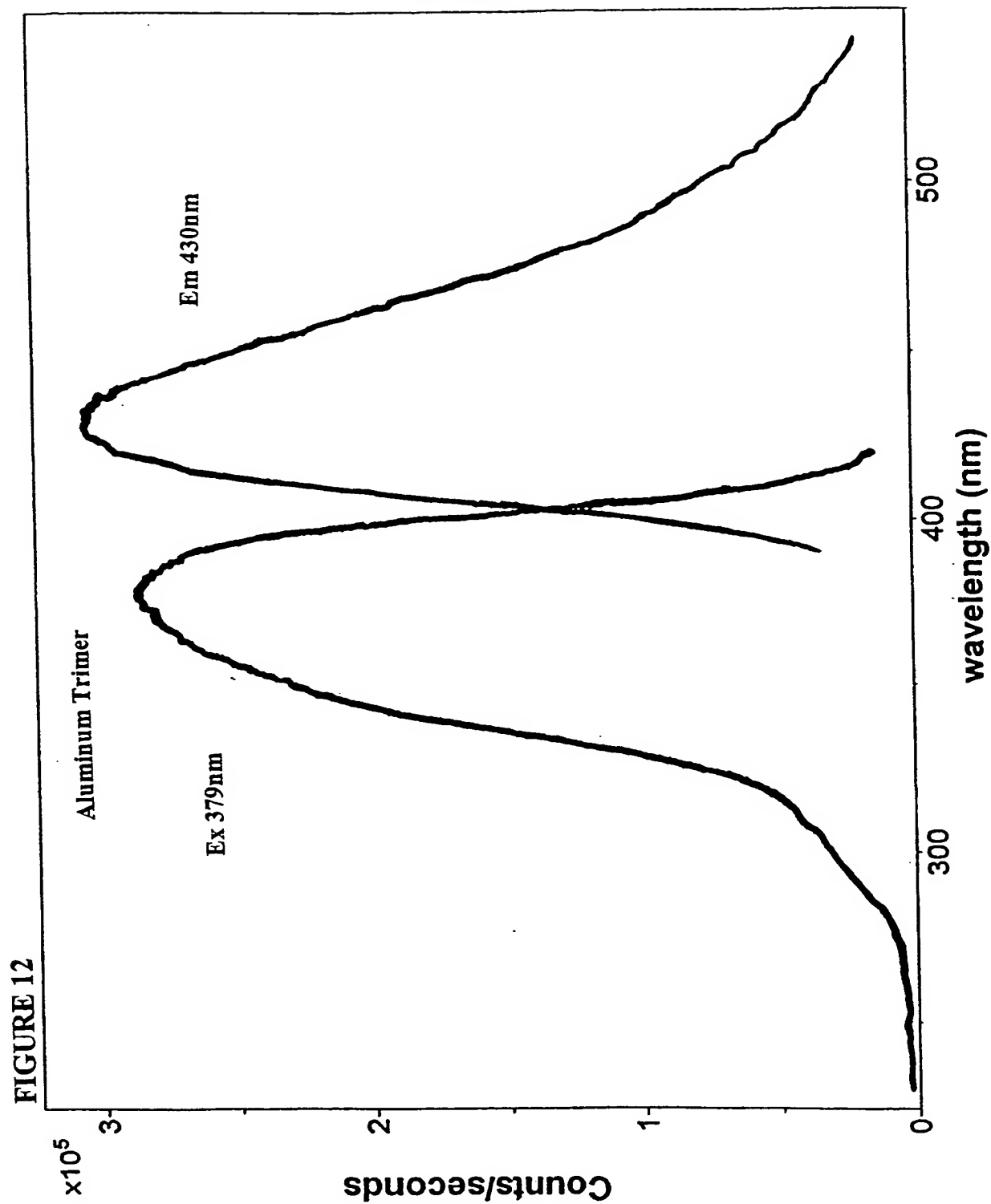
11/28

FIGURE 11



SUBSTITUTE SHEET (RULE 26)

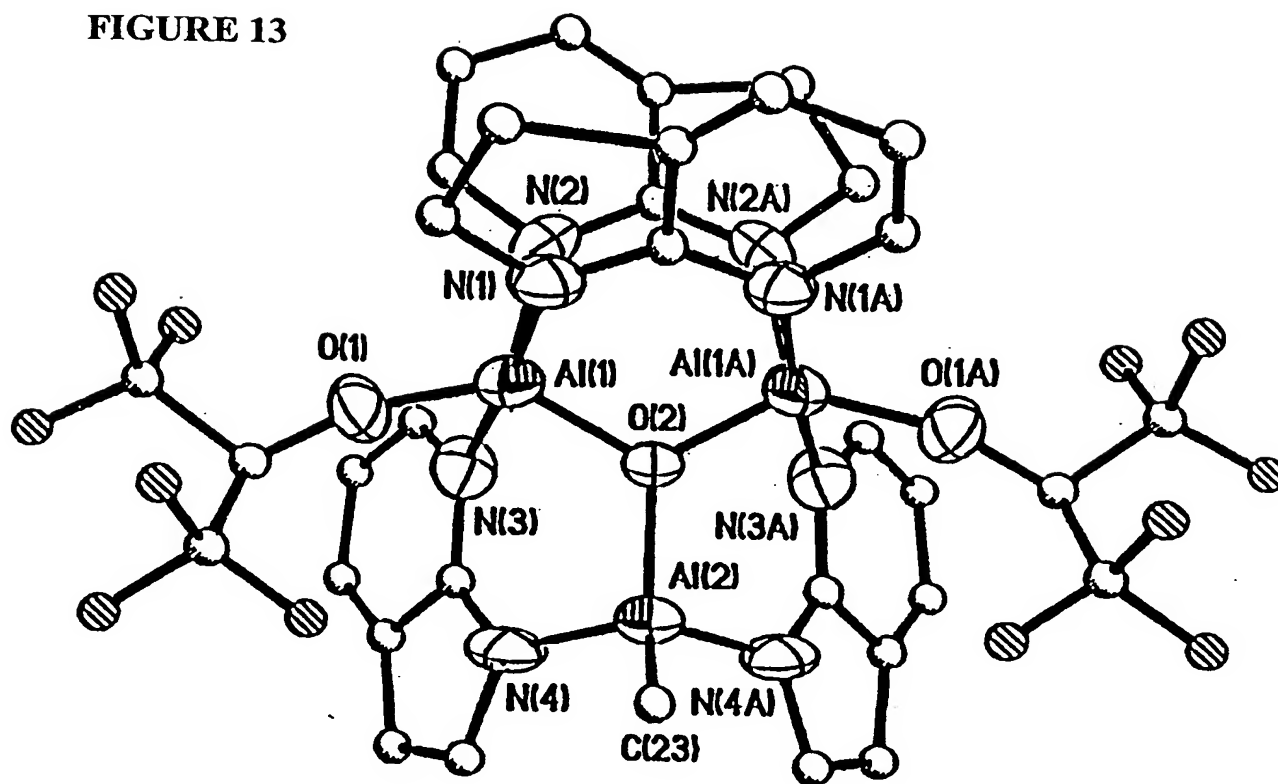
12/28



SUBSTITUTE SHEET (RULE 26)

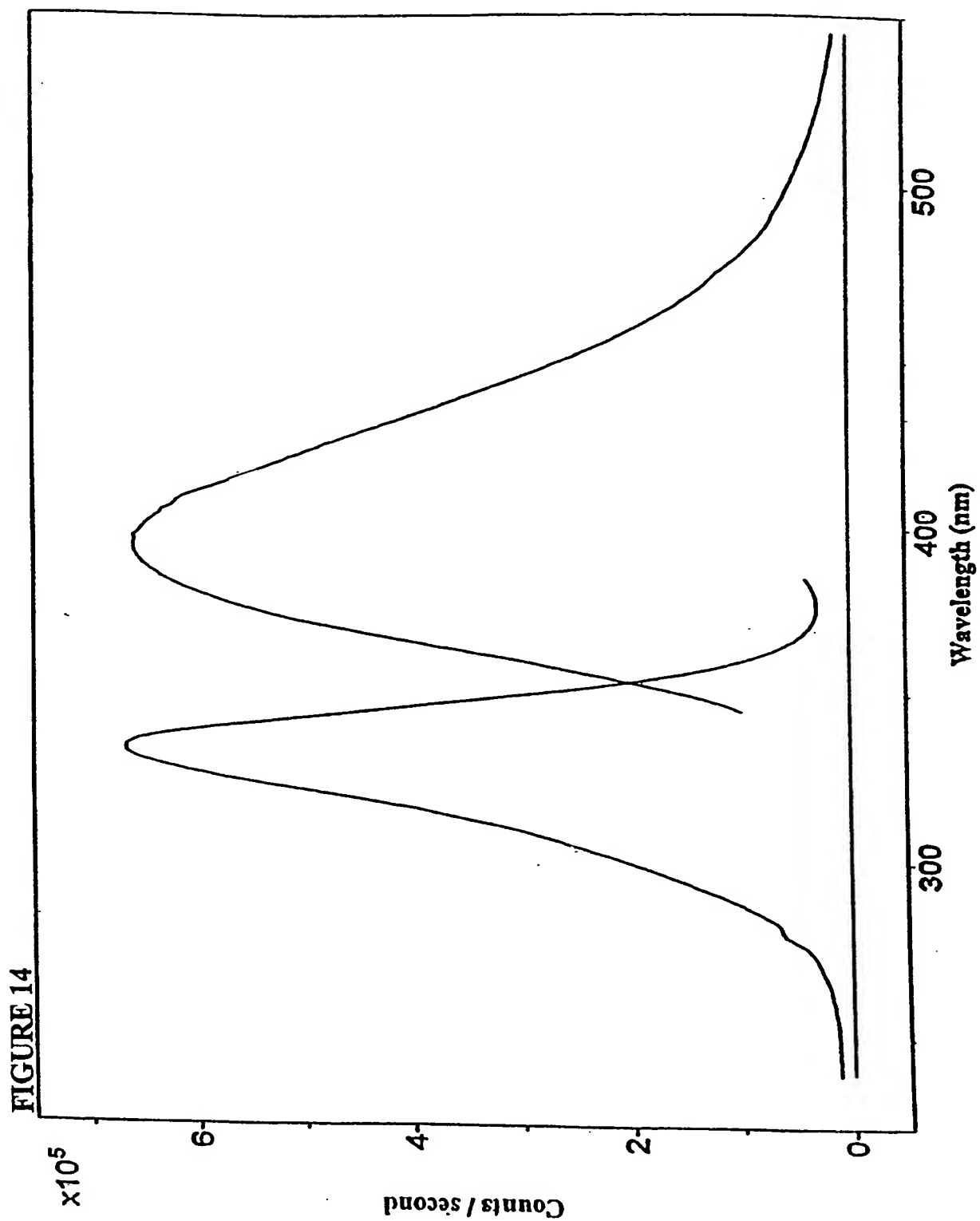
13/28

FIGURE 13



SUBSTITUTE SHEET (RULE 26)

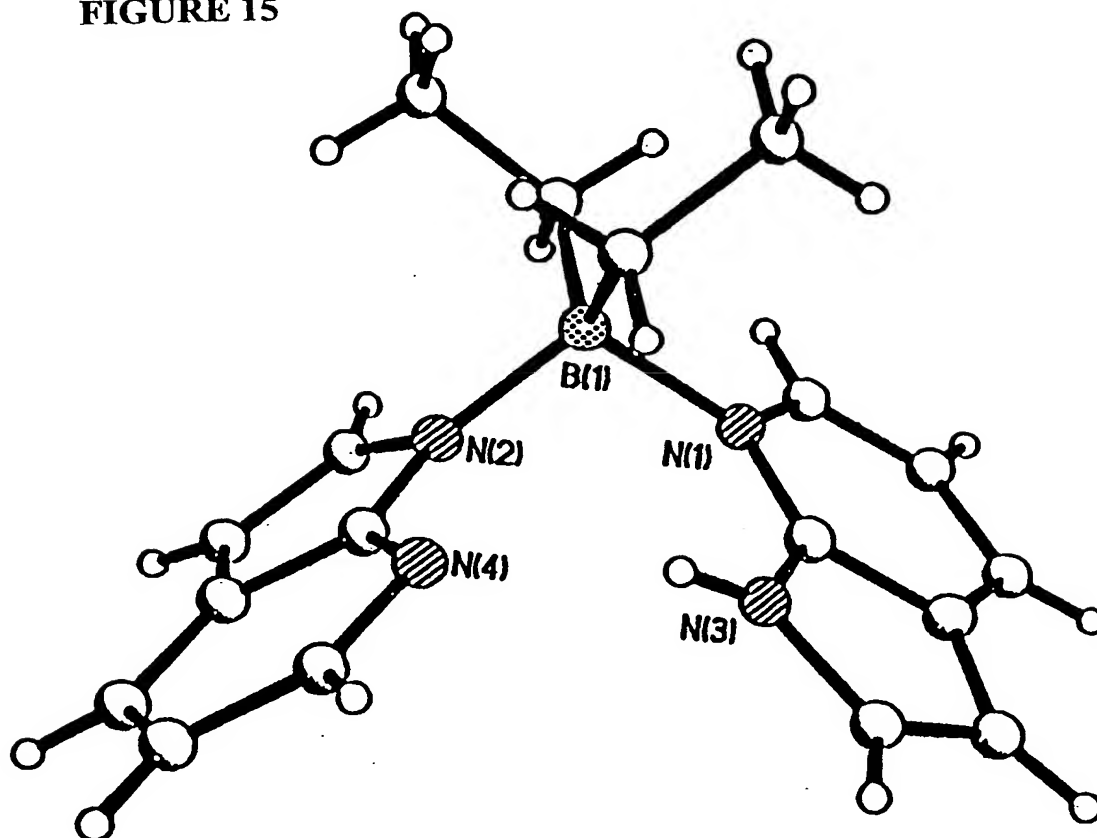
14/28



SUBSTITUTE SHEET (RULE 26)

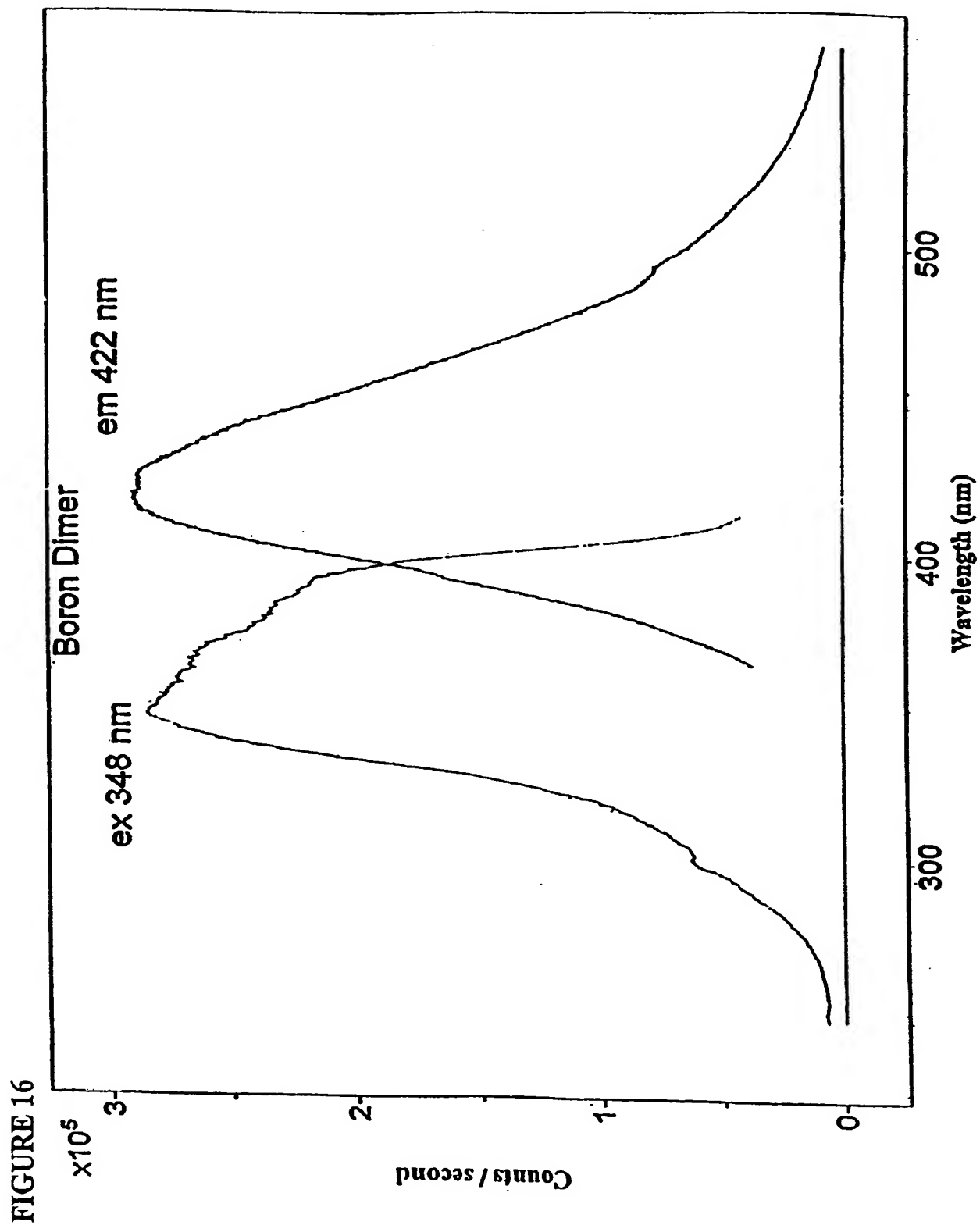
15/28

FIGURE 15



SUBSTITUTE SHEET (RULE 26)

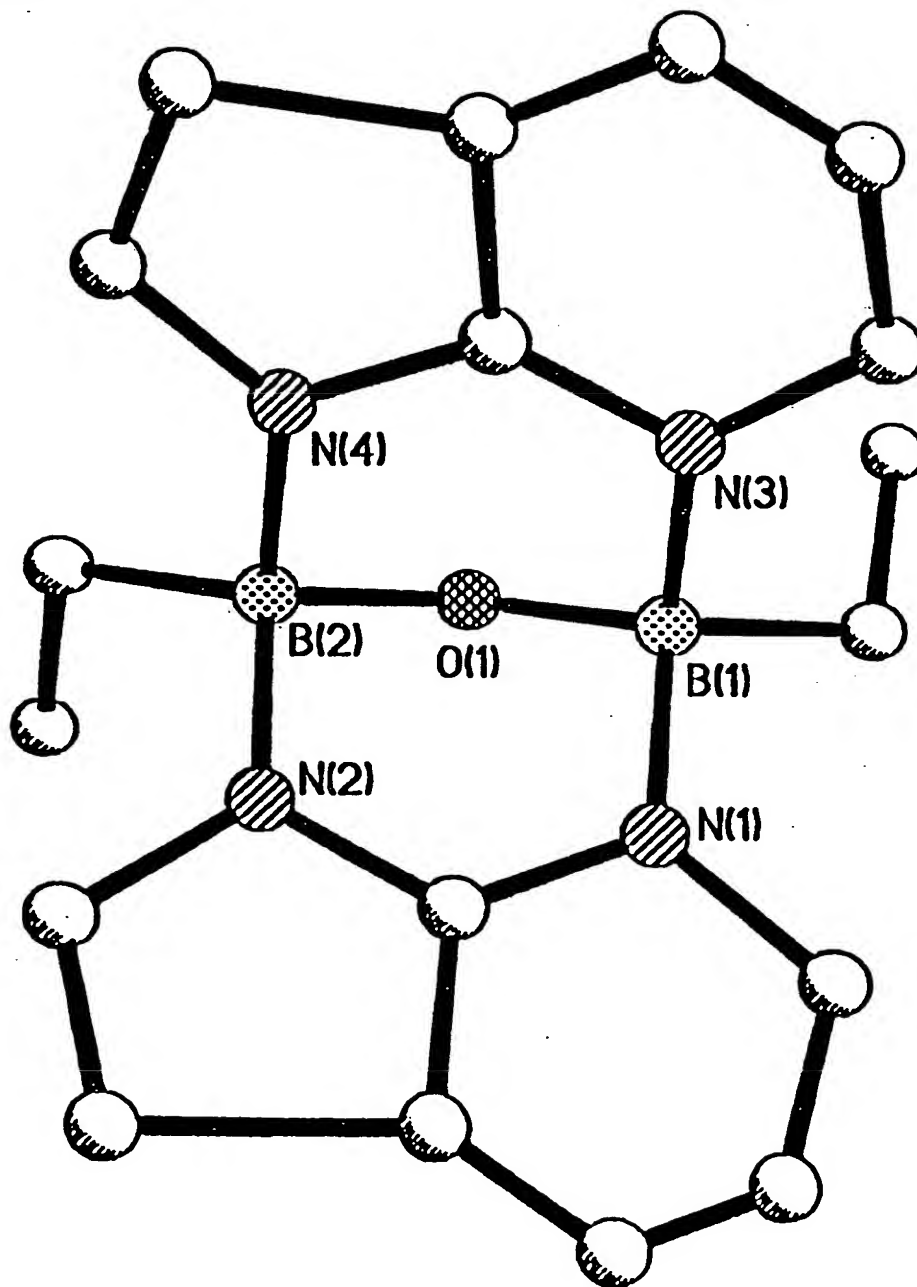
16/28



SUBSTITUTE SHEET (RULE 26)

17/28

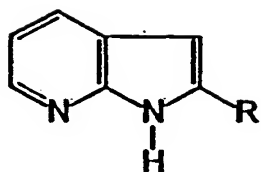
FIGURE 17



SUBSTITUTE SHEET (RULE 26)

18/28

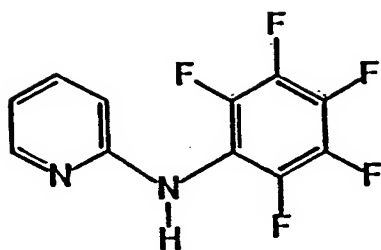
FIGURE 18



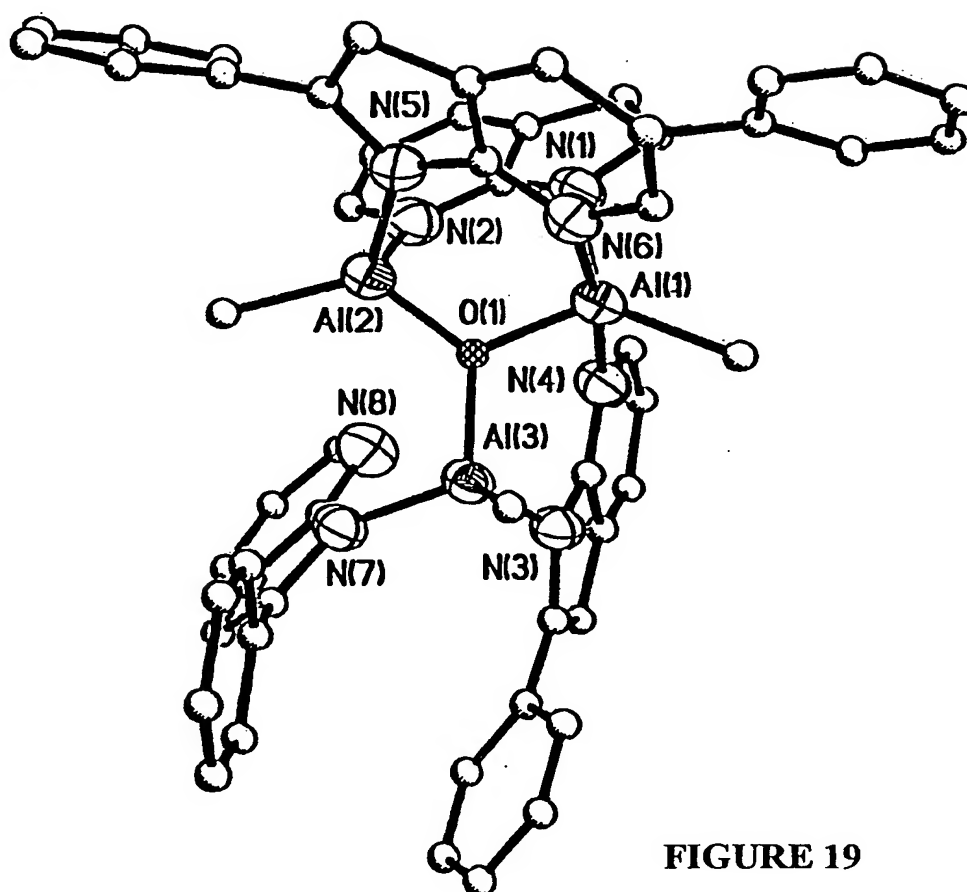
R = Phenyl, Ph-azain

R = Methyl, Me-azain

FIGURE 23

Pentafluorophenyl-2-pyridylamine
(PFPA)

19/28



SUBSTITUTE SHEET (RULE 26)

20/28

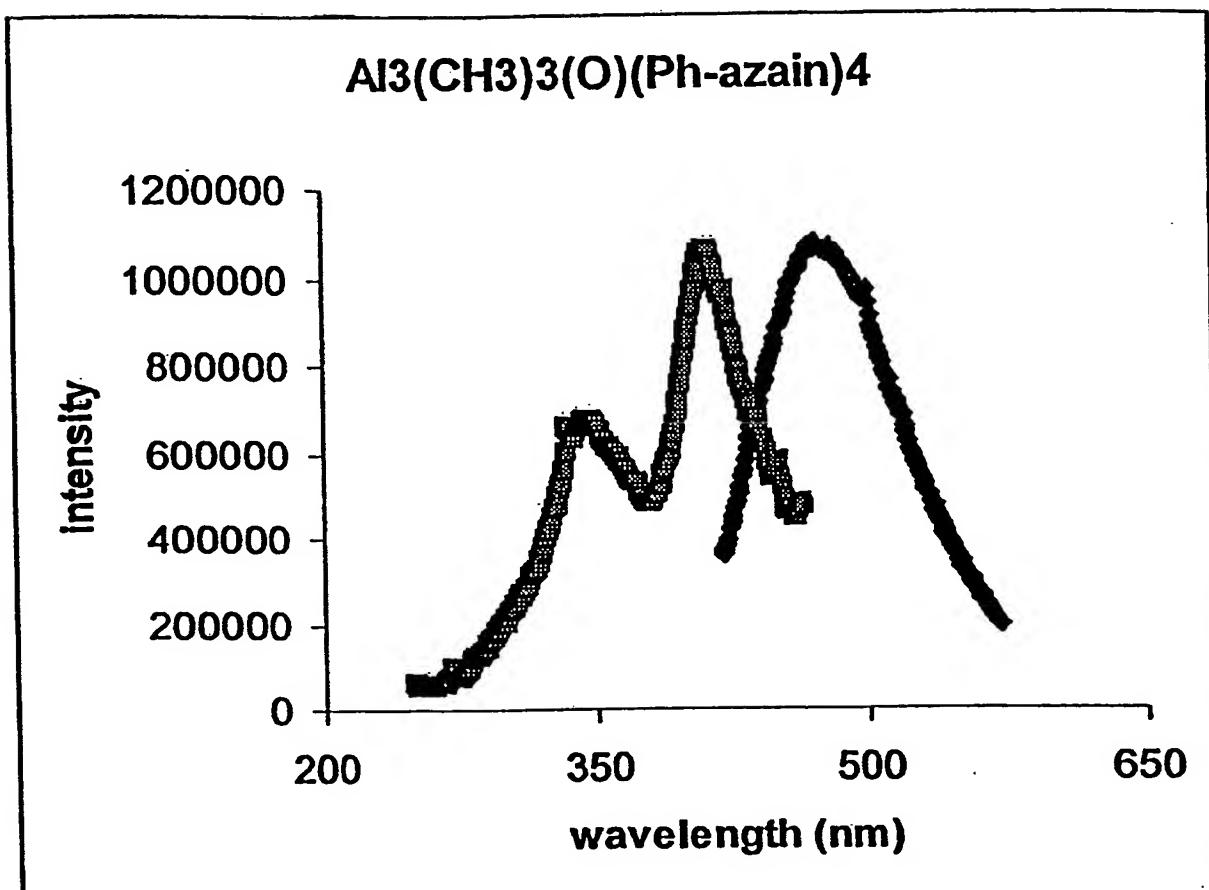


FIGURE 20

21/28

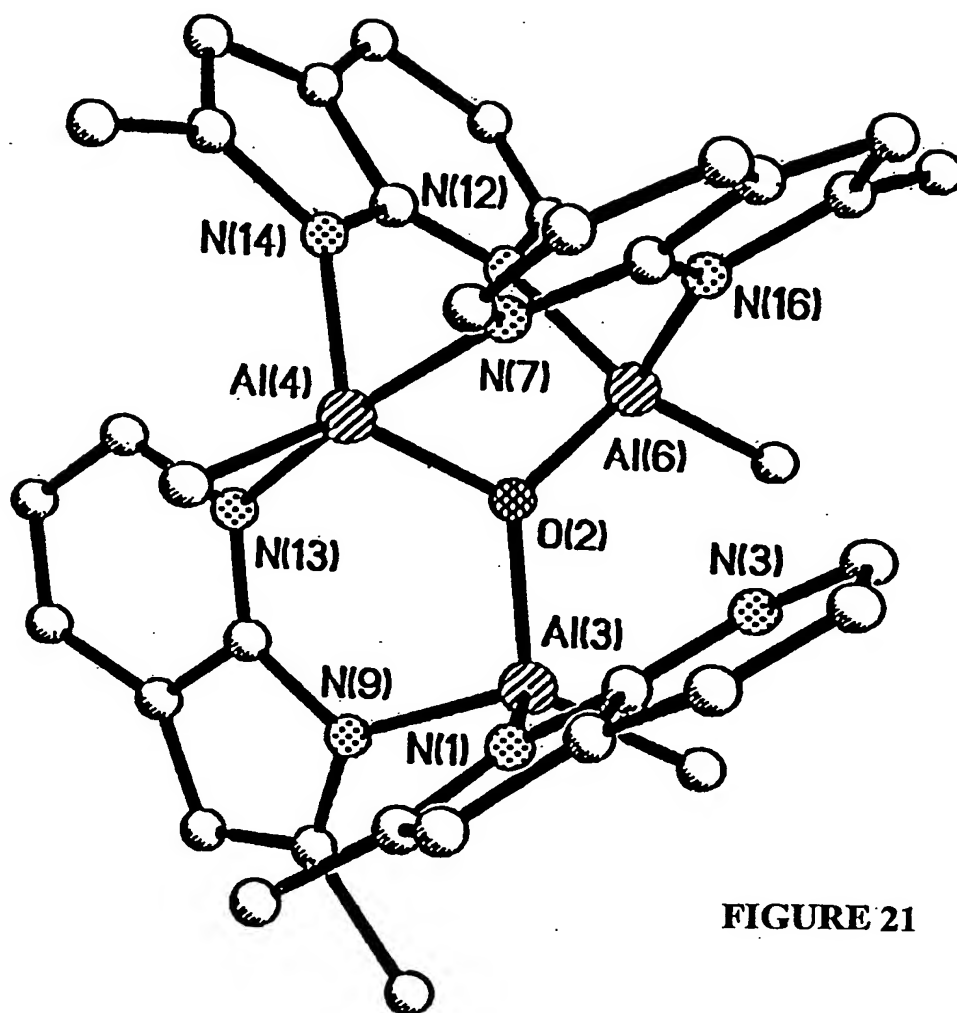
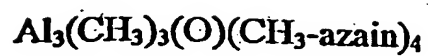
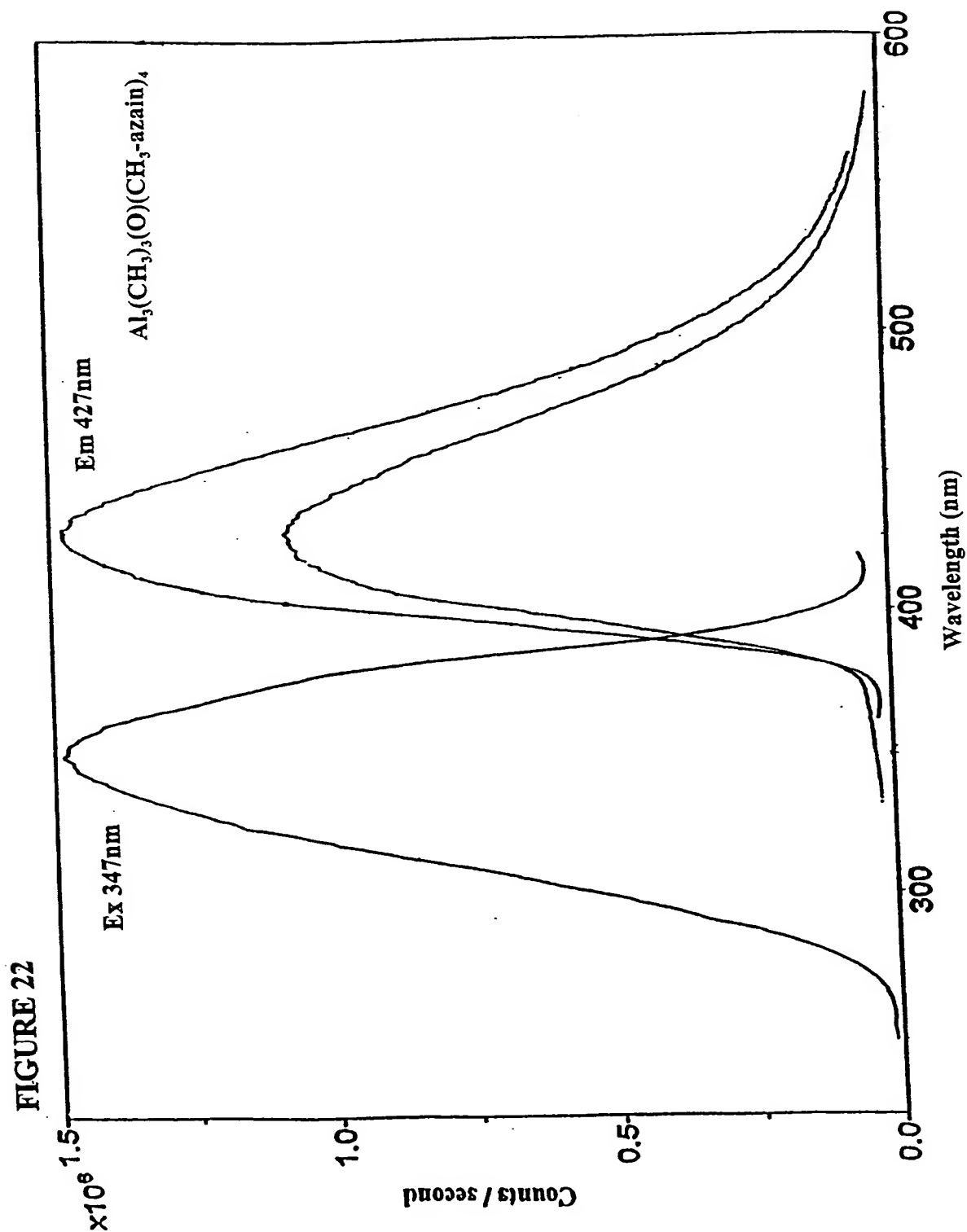


FIGURE 21

22/28



SUBSTITUTE SHEET (RULE 26)

23/28

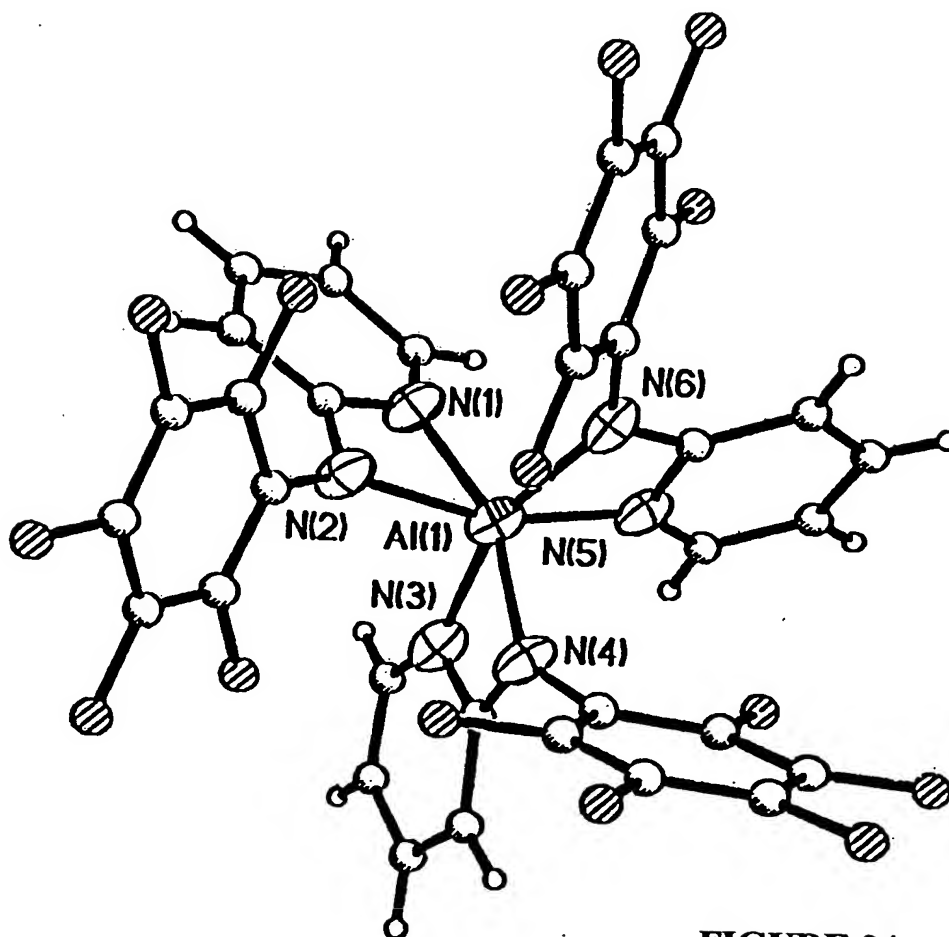


FIGURE 24

24/28

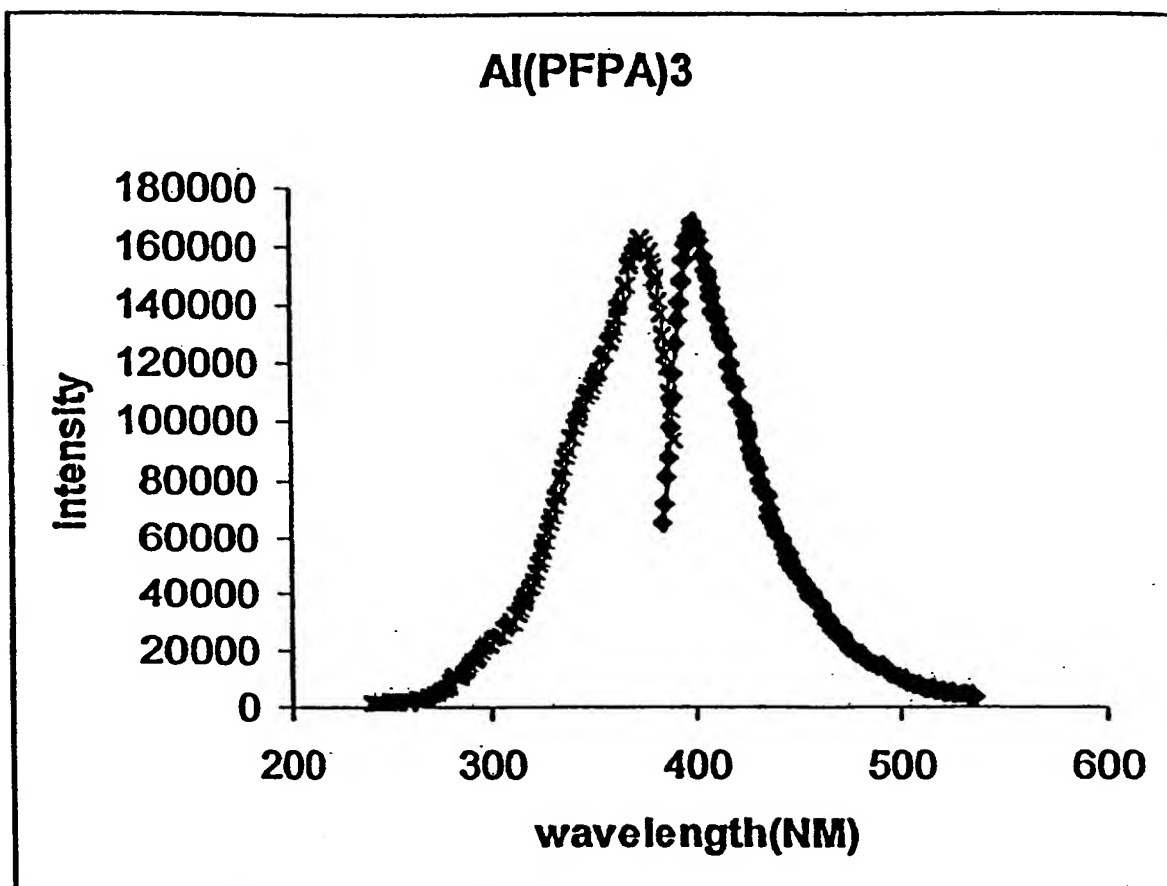
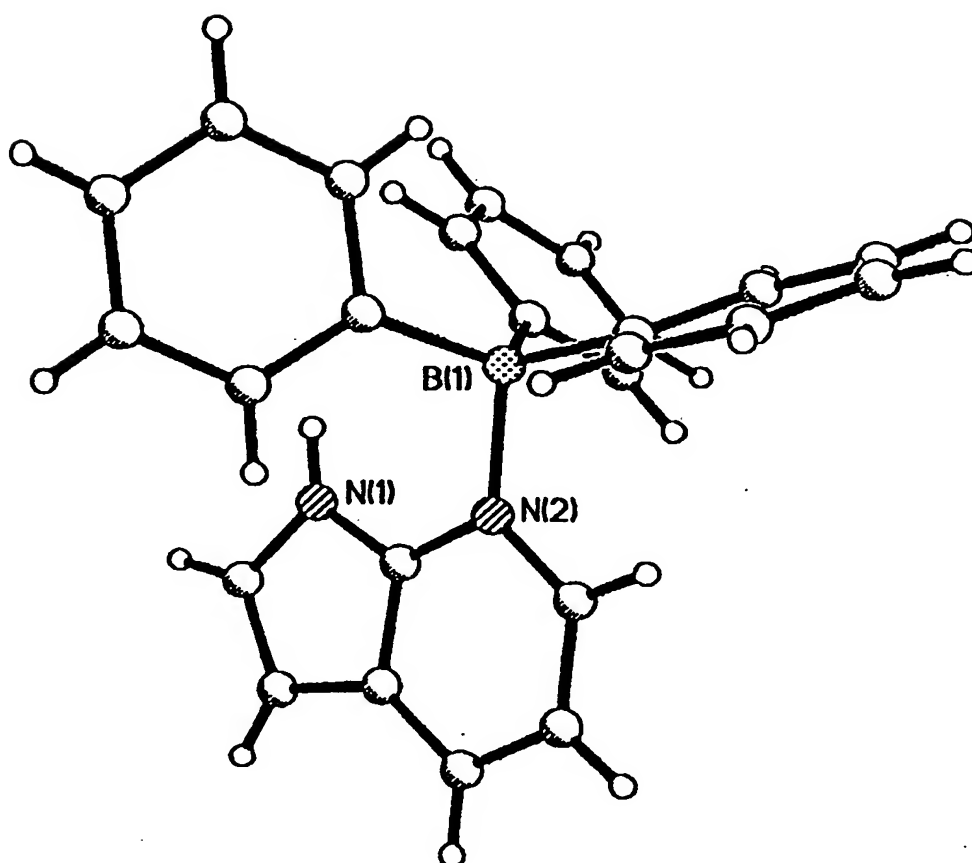


FIGURE 25

25/28

Structure of (7-azaindole)triphenylborane

FIGURE 26



SUBSTITUTE SHEET (RULE 26)

26/28

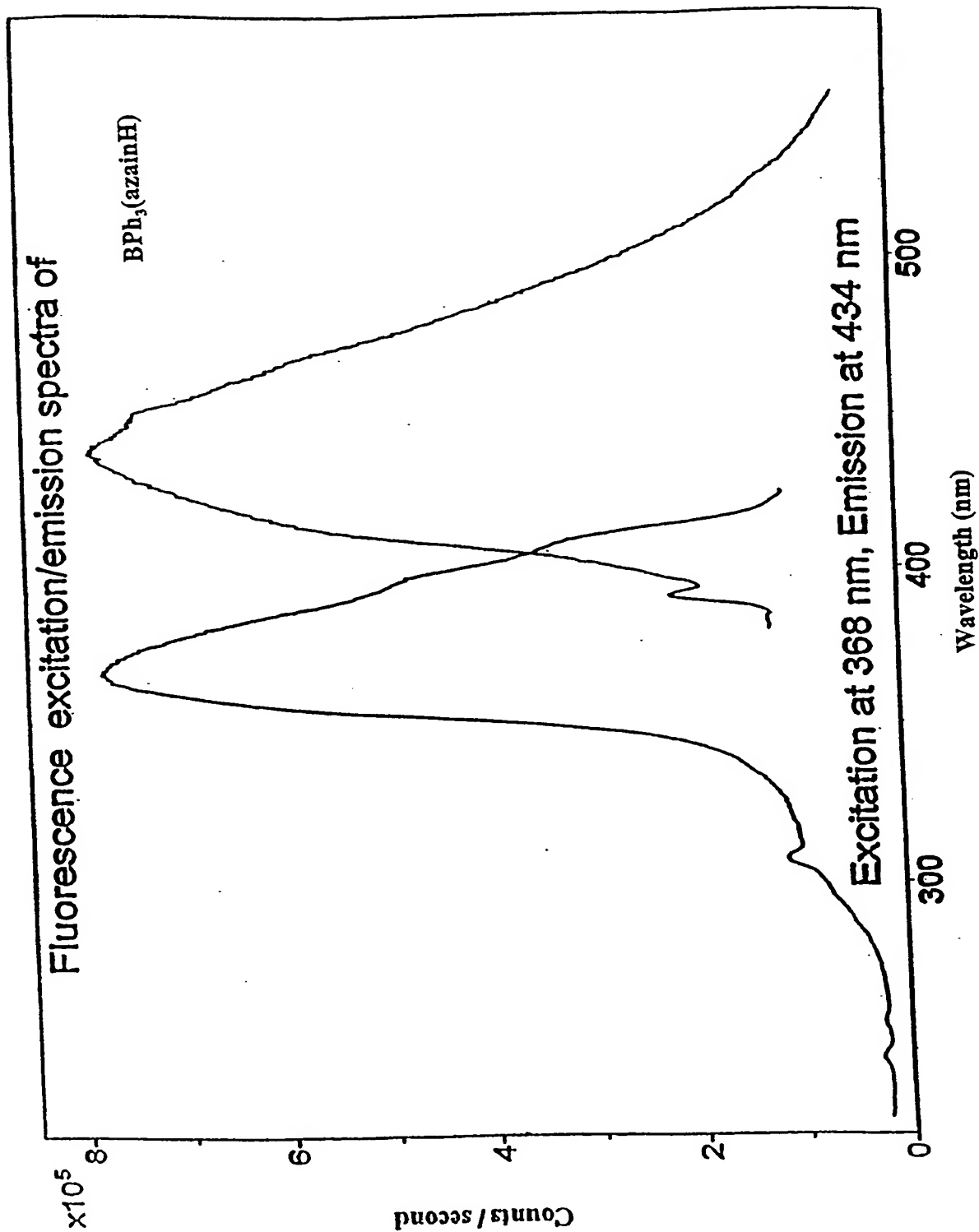
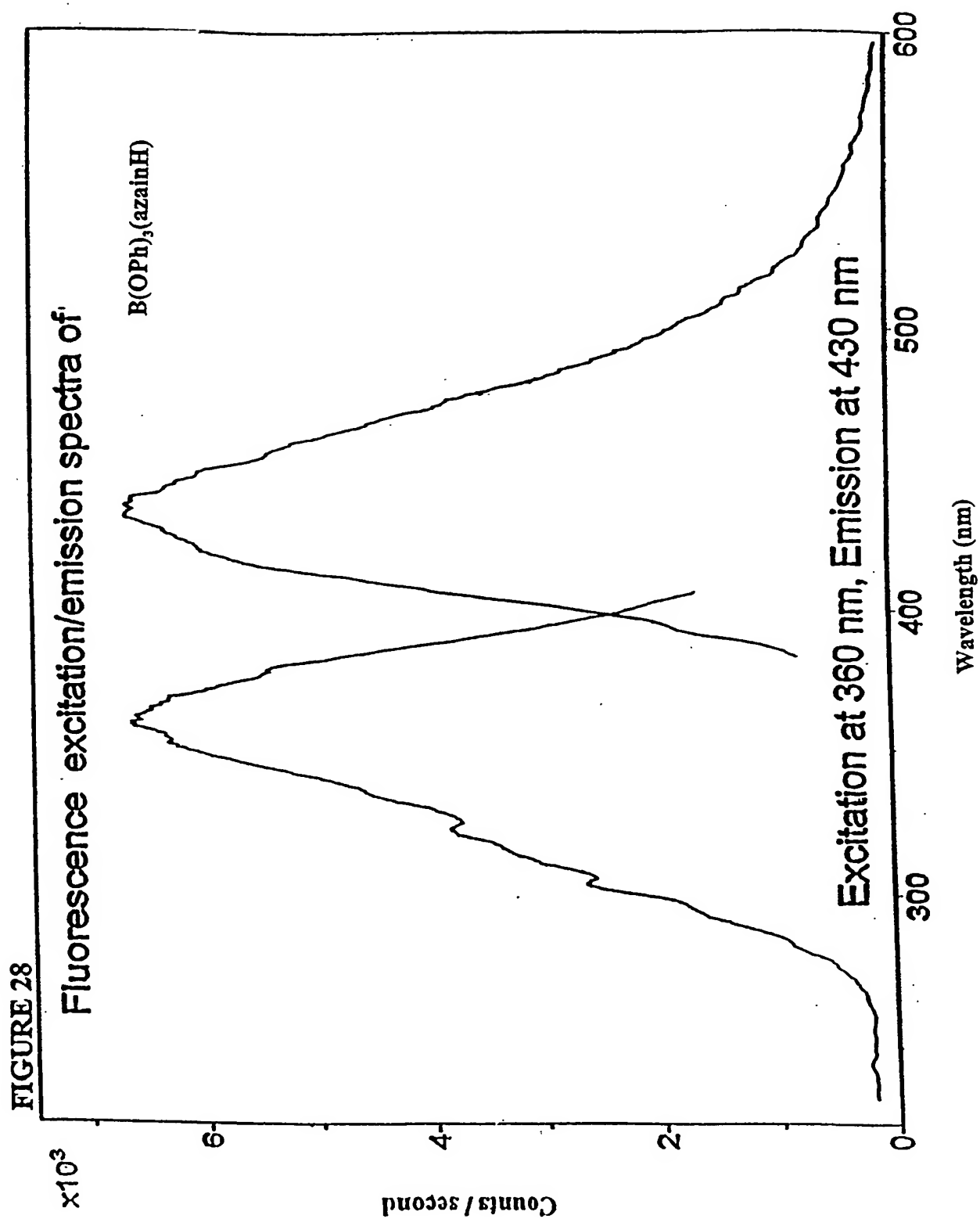


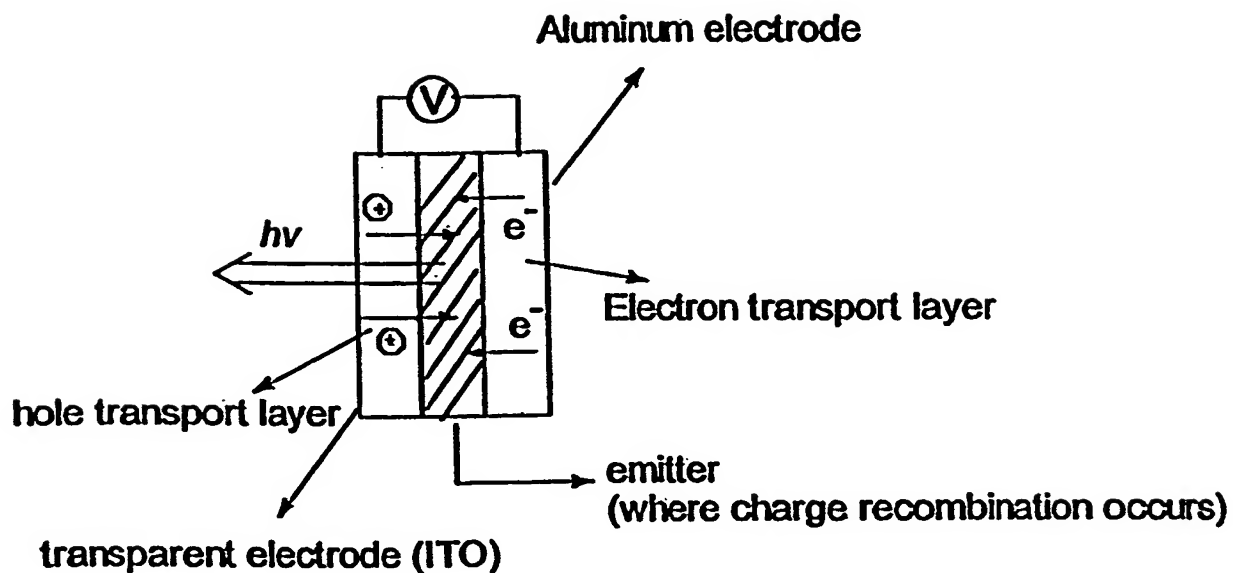
FIGURE 27

27/28



28/28

FIGURE 29



An EL display device

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 98/00100

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K11/06 H05B33/14 C07F5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K H05B C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 579 151 A (EASTMAN KODAK) 19 January 1994 see claims 1-10	1, 18, 19
A	US 5 432 014 A (T.SANO & AL) 11 July 1995 see claims 1-64	1, 18, 19
A	US 5 466 392 A (Y.HIRONAKA & AL) 14 November 1995 see claims 1-15	1, 18, 19
A	US 5 150 006 A (S.A.VAN SLYKE & AL) 22 September 1992 see claims 1-34	1, 18, 19
A	US 5 141 671 A (P.S.BRYAN & AL) 25 August 1992 see claims 1, 18, 19	1, 18, 19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 May 1998

Date of mailing of the international search report

15/05/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Drouot, M-C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: II Application No

PCT/CA 98/00100

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 579151 A	19-01-94	DE 69305262 D	14-11-96
		DE 69305262 T	30-04-97
		JP 6172751 A	21-06-94
		US 5484922 A	16-01-96
US 5432014 A	11-07-95	JP 6033050 A	08-02-94
US 5466392 A	14-11-95	JP 7048385 A	21-02-95
US 5150006 A	22-09-92	AT 111673 T	15-09-94
		CA 2074920 A,C	02-02-93
		DE 69200411 D	20-10-94
		DE 69200411 T	04-05-95
		EP 0534510 A	31-03-93
		JP 5198378 A	06-08-93
US 5141671 A	25-08-92	AT 115617 T	15-12-94
		CA 2086192 A	02-02-93
		DE 69200908 D	26-01-95
		DE 69200908 T	27-07-95
		EP 0525904 A	03-02-93
		JP 5214332 A	24-08-93